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The Behaviour of Sulphur, during Rapid Carbonisation of High-Organic-Sulphur New Zealand Coals

A thesis presented for the
degree of Doctor of Philosophy in Chemical Engineering
in the University of Canterbury,
Christchurch, New Zealand.

by

N. J. PEET

November 1966

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Chap. IV.

Of Iron, and how to transform it into a more worthy metal.

NOw the order of my proceedings requires, that I ſhould ſpeak ſomewhat alſo concerning Iron; for this is a metal which the Wizards of India did highly eſteem, as having in it ſelf much goodneſs, and being of ſuch a temperature, that it may eaſily be transformed into a more worthy and excellent metal then it ſelf is. Notwithſtanding, ſome there are, which reject this metal as altogether unprofitable, becauſe it is ſo full of groſs earthly ſubſtance, and can hardly be melted in the fire, by reaſon of that firm and ſetled brimſtone which is found in it.

Giambattista della Porta,"Natural Magick", Book 5, p.168.
London, 1658

Abstract

Factors relating to the release of sulphur during slow and rapid carbonisation of coals are reviewed in detail.

Experiments are described in which three high-organic-sulphur coals were carbonised in fluid bed and disperse phase equipment. A linear relationship was found to exist between losses of weight and total sulphur. Attempts were made to describe devolatilisation in terms of reaction kinetics, but with no real success; rate-controlling steps are evidently of a physical, rather than a chemical nature.

Hydrogenation for short periods was effective in lowering the sulphur content of chars, without appreciably affecting the yield.

Analysis of the volatile products showed that most of the volatilised sulphur is present as mercaptans or high-molecular-weight tarry compounds.

Acknowledgments

This work has been carried out under the direction and supervision of Professor S. R. Siemon and Dr J.B. Stott, to whom the writer expresses grateful thanks for their experience and gentle guidance. The writer also acknowledges the assistance and encouragement of Professor A. M. Kennedy and the other members of staff of the Chemical Engineering Department.

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Contents

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I. Introduction

The need for adequate supplies of high quality metallurgical coke has been highlighted by the plan for the setting up of an iron and steel industry in New Zealand, and also by the possibility of a substantial export trade with Japan. At present, the relatively small demand (ca. 6,000 tons/annum) for metallurgical coke for use in foundries is met by the output of one company[73], but the probability of a greatly increased future demand led Hughson[73] to investigate the reserves of coking coal in New Zealand, and the feasibility of producing metallurgical coke in much larger quantities (e.g. ½-1 million tons/annum), both for home use and for export.

In New Zealand, reserves of coking coals are virtually confined to the Greymouth and Buller coalfields, on the West Coast of the South Island, where in 1959[73] such reserves were estimated to total some 77 million tons.

Unfortunately, a considerable portion of these reserves suffers from the disadvantage of a medium or high sulphur content. Hughson classified these coals, according to their sulphur contents, and found that low sulphur coals (less than 1% total sulphur) constituted 46% of reserves, medium sulphur coals (1-2.5% total sulphur) 23%, and high sulphur coals (more than 2.5% total sulphur) 31% of reserves. 'As a general rule for New Zealand coals, the percentage of sulphur in the coke will be about the same as that in the coal[74] (when coked by conventional methods), and since requirements for metallurgical coke normally

specify a maximum sulphur content of 1%, the coal charged to the coke oven must not exceed 1% sulphur. It is possible to use medium sulphur coals, by blending with very low sulphur coals, but even so it appears that only about half of the reserves of coking coals can be used for the production of metallurgical coke, by present methods.

Since, almost without exception, the other one-third of coals of higher sulphur content (mainly in the Buller area) are otherwise of the highest quality, an investigation into the possibility of production of low sulphur coke from these high sulphur coals would seem to be both relevant and timely.

Sulphur in coal occurs mainly in three forms[144]: pyritic sulphur, FeS_2, as iron pyrites or marcasite; sulphate sulphur, usually calcium or iron sulphate; and organic sulphur, in which the sulphur is chemically bonded within the complex "molecules" of which the coal substance is comprised. (According to one author[83], the majority of organic sulphur is, in fact, nothing but very finely dispersed pyrite; experiments carried out by other workers[24,148] do not support this claim, although there is little doubt that present methods of analysis for pyritic sulphur in coal are not capable of detecting all such sulphur, particularly when present in micro-crystalline form in hard coals[18,47,102].) Some free sulphur is often found[159], usually in minute quantities.

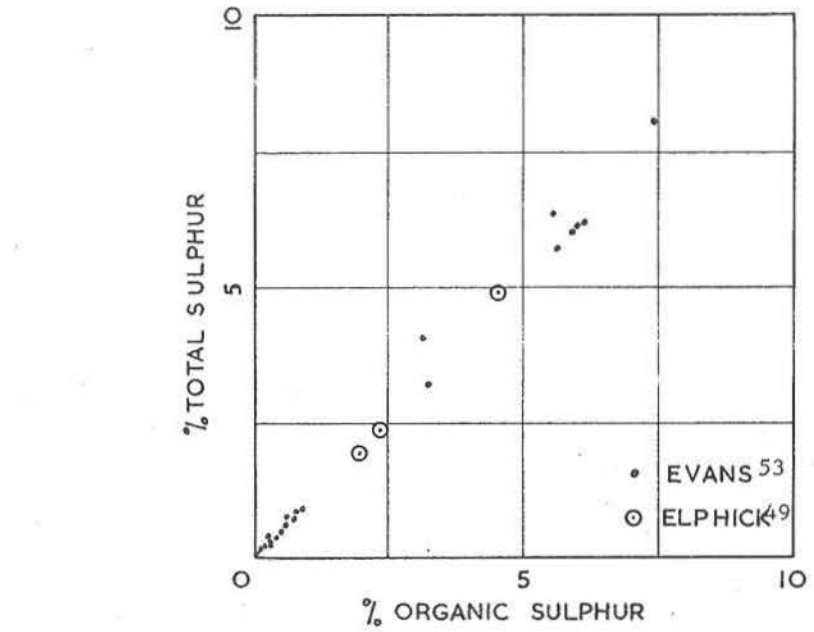
New Zealand coals are unusual in that, unlike most coals found elsewhere in the world, the sulphur contents are mainly

organic[48,53,75,140,152] (Fig. 1). Data quoted by Hughson[73] and Suggate[140] on the distribution of the different forms of sulphur indicate that the organic sulphur content normally exceeds 90%, the remainder being mainly pyritic sulphur. This may be compared with coals from the U.K. and U.S.A. in which the pyritic sulphur content normally exceeds 50% of the total sulphur, and occasionally exceeds 90%.

Since organic sulphur is not capable of being removed by washing, which is the method generally used for removal of mineral sulphur, it is necessary to determine what other processes are available, capable of removing organic sulphur, either before, during, or after coking, to enable a low sulphur coke to be produced from a high sulphur coal.

Such processes must, of necessity, involve some modification of the chemical structure of the coal, in order to release the organic sulphur from its chemical bonds, and it is the purpose of the present work to investigate promising methods, with a view to obtaining information and data from which the feasibility of large-scale desulphurisation might be determined.

Another relevant factor is that sulphur would presumably be produced from such processes as a by-product. New Zealand's present imports of sulphur are about 200,000 tons per annum[39], and the recovery of sulphur from coking of high-sulphur coals would go some way towards alleviating the shortage of this valuable raw material.



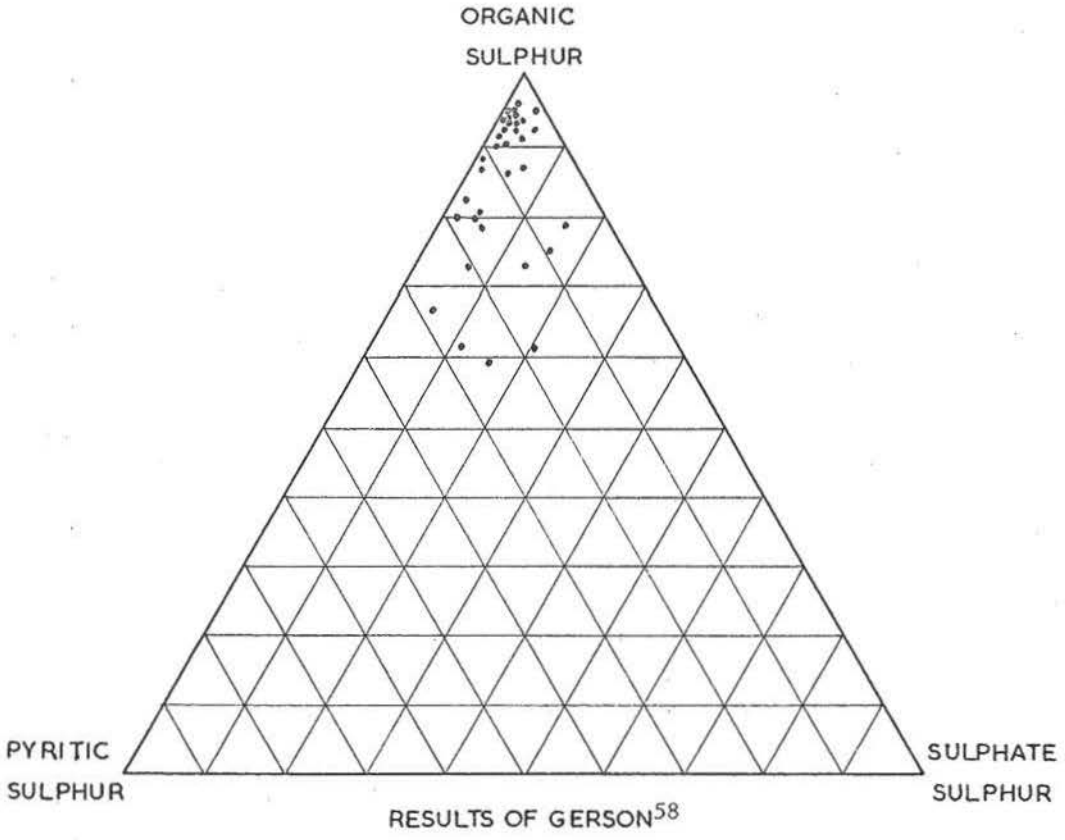


FIGURE 1 FORMS OF SULPHUR IN NEW ZEALAND COALS.
(REDRAWN FROM SUGGATE[140])

II. Origin of Sulphur in Coal

Sulphur in coal is presumed to derive from two main sources: sulphur in the coal-forming plants[23,54,66,144], and sulphur extracted by the coal seam from sea-water[66,83,140,153,158].

Sulphur is an element essential for plant growth, and occurs in proteins and in certain waste and protective substances. During decay of the plants in the bog, these sulphur-containing compounds are destroyed, releasing much of the sulphur as hydrogen sulphide, which may escape or alternatively may be chemically combined within the bog by combination with iron compounds, by absorption in organic coal-forming materials, or by bacterial action.

Recently, it has been established, both in the U.K.[149] and U.S.A.[154], that where the coal seam is closely overlain by marine beds, the sulphur content of the coal is generally high, whereas if the stratigraphic distance between the seam and the base of its nearest overlying marine bed is large, the sulphur content of the coal is low. In New Zealand this view has been substantiated by a geological survey of the Greymouth coalfield in which Wellman[66,152] found that sulphur contents from a bore near Millerton ranged from 7.5% (d.a.f.) immediately below the marine overlay to 2.1% at 65 feet below the overlay. A similar decrease has been demonstrated in other New Zealand coalfields[140] (Fig. 2). It would appear, therefore, that a substantial amount of sulphur is extracted

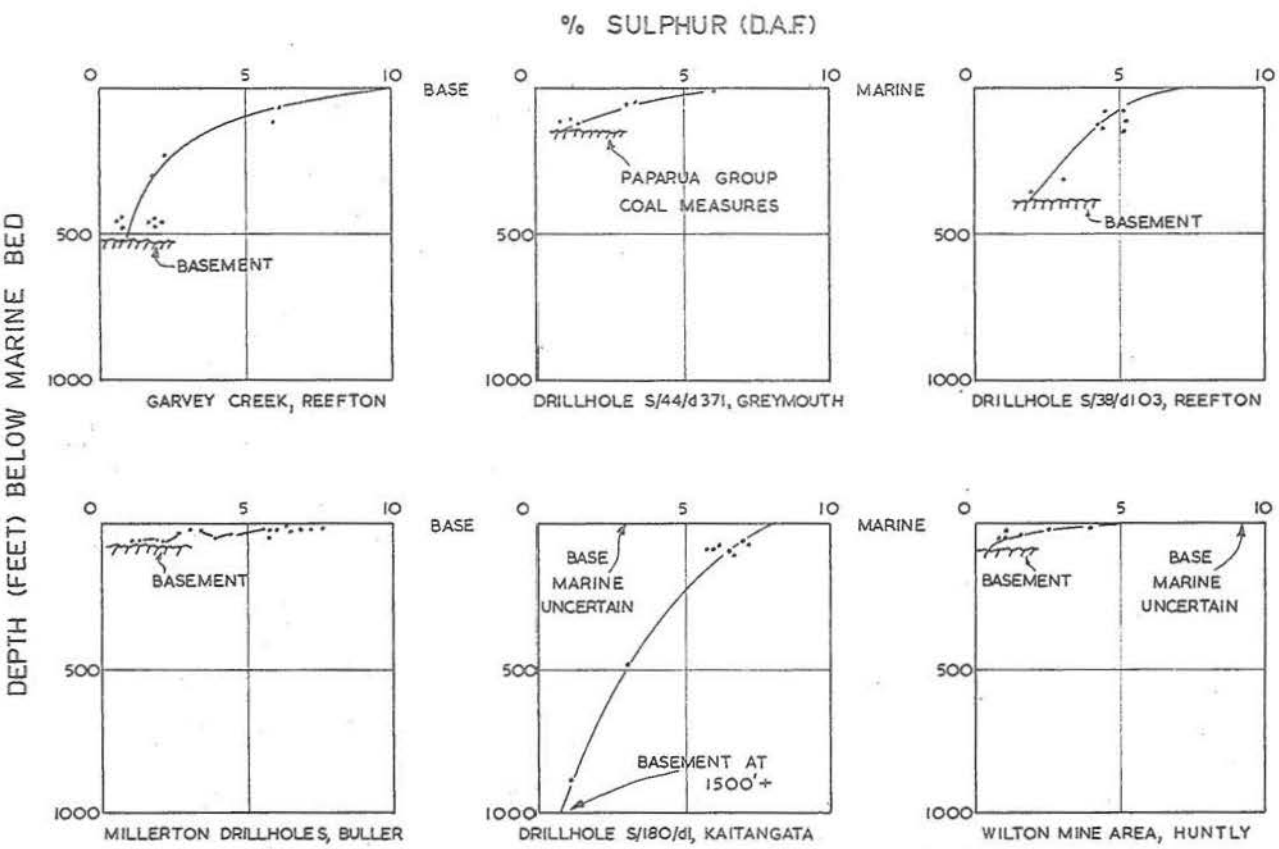


FIGURE 2 SULPHUR CONTENT IN RELATION TO STRATIGRAPHIC DEPTH BELOW MARINE BEDS.

(REDRAWN FROM SUGGATE[140])

from sea-waters permeating the coal bed after its burial.

On the other hand, it is also interesting to note that percolating ground water is capable of significantly reducing the sulphur content of the coal seam, as discussed by Suggate[140] in his review of the geology and properties of New Zealand coals.

III. The Nature of Organic Sulphur in Coal

Very little is known about the nature or distribution of organic sulphur compounds in coal, and what work has been done (mainly restricted to certain high-sulphur coals found in India and Yugoslavia) has only indicated the types of linkage that may be present, joining sulphur with the rest of the complex coal molecule. The present state of knowledge in this field has been well summarised in a review by Mapstone[99] from which much of the material in this section was obtained. (Also see Brooks[23], Given and Wyss[60], van Krevelen[87], Theissen[144], and Ahmed[2].)

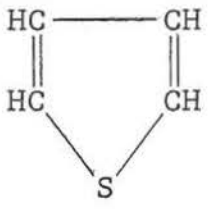
Although many organic sulphur compounds are known, very few are likely to be found in other than trace quantities in coal, either due to their instability in the presence of air and water, or because they require conditions for their formation unlikely to have been encountered during the coalification process. The types of organic sulphur compound assumed to be present in the coal mass, and for which some confirmatory evidence is available, include

(a) mercaptan or thiol, RSH

(b) sulphide or thioether, RSR'

(c) disulphide, RSSR'

(d) aromatic systems containing the thiophene ring,



(R and R' being alkyl or aryl groups; in (b) and (c) both may be part of one ring system.)

Solvent Extraction Studies

According to van Krevelen[87], since chloroform and pyridine extracts and extraction residues have similar sulphur contents, it may be concluded that organic sulphur compounds are distributed uniformly throughout the coal as part of its fundamental constitution. As a corollary of this, it is not unreasonable to expect that a study of the solvent extracts of coal would yield information of value as to the nature of organic sulphur in the original coal. Bhatnagar and Dutt[19] have detected mercaptans and disulphides in the solvent extracts of coals. Dibenzthiophene has been isolated from the aniline extract of a coal by Gusev[64], who suggests that the circumstances under which it was found indicate that it must have existed as such in the original coal. This is claimed[99] to be the only direct evidence of the occurrence of a thiophene ring in coal.

The amounts of organic sulphur present as thiol, sulphide, disulphide and thiophene groups have been determined by Roy[127], who analysed benzene and ethylene diamine extracts of two Indian coals. Results are summarised in Table 1.

Table 1

Solvent	Coal	Thiol %	Sulphide %	Disulphide %	Thiophene %
Benzene	I	53.1	26.7	2.5	5.6
	II	58.6	31.6	1.9	3.2
Ethylene diamine	I	54.8	27.1	2.8	4.8
	II	60.2	29.9	2.3	3.1

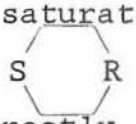
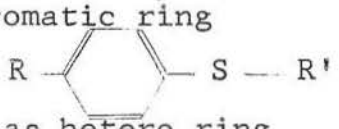
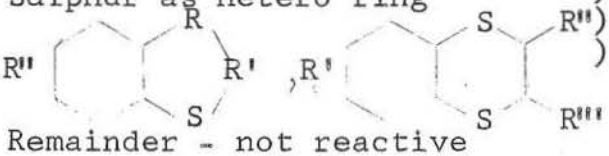
Notes: (i) Coal I - Baragolai 3, total sulphur 4.84%, organic sulphur 4.57%.
Coal II - Cherrapunji, total sulphur 8.71%, organic sulphur 6.95%.

(ii) Thiol groups include aliphatic and aromatic thiols. No non-aromatic sulphides were detected.

(iii) All results are based on the percentage of total sulphur in the coal.

Miura and Yanagi[107], in a similar type of study on the solvent extracts of a Japanese coal (Miike C, organic sulphur content 2.95%), used benzene, tetrahydrofuran (THF) and dimethylformamide (DMF) solvents. Their results are summarised in Table 2.

Table 2

Sulphur Linkage	% S in Solvent Extract: DMF	THF	Benzene
Thiol -SH	8.72	3.00	5.28
Disulphide -S-S-	5.62	12.16	12.77
Sulphide not directly combined with aromatic ring -S- / Sulphur as saturated hetero ring 	32.00	37.21	27.94
Sulphide directly combined with aromatic ring  / Sulphur as hetero ring 	18.69	17.47	6.64
Remainder - not reactive	34.97	30.16	47.37

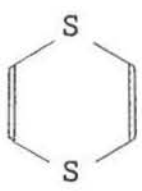
Other Studies

Oxidation studies by Horton and Randall[68] have shown that about half of the organic sulphur in coal can be easily oxidised to sulphate, even when the proportion of original carbon oxidised is small. Iyengar et al[77] oxidised high-sulphur coals with air and nitric acid, and obtained sulphonic acids. They concluded that part of the sulphur was present as thiocarbonyl groups ($>C = S$), and that the coals studied contained little sulphide sulphur.

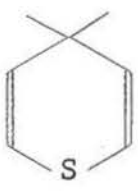
From a study of the carbonisation of coal in the

presence of superheated steam, Lissner and Nemes[94] stated that organic sulphur in coal exists in four forms: $\geqslant$C-SH and $\geqslant$C-S-S-C$\leqslant$ groups (probably attached to nitrogen), and $>$CH-SH and $>$CH-S-CH$<$ groups. The evidence should be regarded as indicative, rather than conclusive, but such structures are certainly feasible.

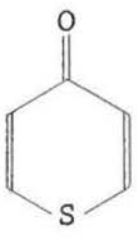
The existence of thiol, sulphide and disulphide groups has also been demonstrated by the reactions of coal with methyl iodide[3,33,63,148]; according to Gusev[63], these groups are probably of a complex alkyl or alkenyl (ethylenic) form. Since thiophene does not react with methyl iodide, the organic sulphur remaining after treatment with this compound is claimed to be exclusively thiophenic in nature, but this argument would similarly apply to alkyl aryl sulphides, diaryl sulphides[99], and to compounds in which the sulphide linkage forms part of one ring. As has been shown by Jones[81], six-membered heterocyclic sulphur rings have quite enough stability to be formed and preserved during coalification, and these structures are just as probable as systems containing the thiophene nucleus. Structures suggested include the 1,4-dithiadiene (a), 4-thiopyran (b), and 4-thiopyrone (c) systems:



(a)



(b)



(c)

As a result of experiments involving the heating of coals with sulphur at 130°C, Postowsky and Harlampovitch[119] concluded that biothioether structures (R-S-C-C-S-R', where R and R' are not aryl) could be present in coal. Gusev[63] later confirmed this suggestion from a study of the reactions of cupric chloride with coal sulphur. A criticism of Gusev's method has been noted by Mapstone[99].

A method for the determination of the thioether group, based on its selective catalytic decomposition in the presence of alumina at high temperature, has given rise to the suggestion by Wnekowska[4,155] that the organic sulphur in coal consists only of thioether and thiophenic groups, and that the ratio thioether/thiophenic sulphur decreases from 3:1 in high-volatile coals to 1:6 in semi-anthracite.

To summarise, it appears probable that the two main forms of sulphur in coal are heterocyclic ring compounds, in which sulphur has replaced carbon, and side-chain thioether compounds, in which sulphur has replaced oxygen. The relative proportions of these two forms vary considerably, but it seems that as the rank (i.e. carbon content) of the coal increases and the aromaticity increases, the greater is the proportion of sulphur present in ring compounds. It is important to realise, however, that there is no positive evidence for the existence of heterocyclic sulphur linkages in coal; at the present state of knowledge, their presence can only be inferred.

However, it should be noted that cyclic sulphides, thiophenes, benzothiophenes, dibenzothiophenes and thienothiophenes have been identified in crude petroleum, as well as thiols, aliphatic sulphides, and disulphides [35,67,145]. Since both coal and petroleum are derived from living matter, and since there appears to be a strong correlation between coal sulphur content and the presence of overlying marine beds, it is not unreasonable to infer that, by using the techniques developed for the investigation of oil sulphur, heterocyclic sulphur compounds may yet be shown to be present in coal.

Much work still remains to be done on the composition of the various organic sulphur compounds in coal, one important requirement being the development of means of accurately distinguishing between the aromatic and aliphatic sulphur in the coal structure. The separate effects of these two main forms of sulphur on coal properties (e.g. rank, swelling number) are still largely unknown.

IV. The Properties of High-Organic-Sulphur Coals

There are very few coals whose organic sulphur contents are sufficiently high to affect the physical and chemical properties of the coal to any great extent. Such coals have been reported only from Rasa (Yugoslavia)[86] (organic sulphur content 11.9% (d.a.f. basis)), Assam (India)[22,33,59,61,78,126,127] (6.95%), Tangorin (Australia)[100] (6.5%), and New Zealand[140] (8-9%, possibly higher). Coals of high total sulphur content are also found in Pakistan[78] (10%), Russia[3] (9%), and Borneo[78] (5%), although in these coals much of the sulphur is in the mineral form.

From a consideration of molecular structure, it is to be expected that a high-organic-sulphur content would have a significant effect on the rank of a coal, by virtue of the ability of one atom of sulphur to replace two carbon atoms (as in a thiophene ring) or one oxygen atom (as in a thioether group). The coal from Rasa[86] contains 11.9% organic sulphur, and has many abnormal properties, some characteristic of a lignite, and others indicating a bituminous coal. According to Kreulen[86], this dual character is explained when, by adding the sulphur and oxygen contents, a value close to the oxygen content of a lignite is found; by adding sulphur and carbon the figure is that of the carbon content of a bituminous coal. On the evidence available at present, it is not possible to decide whether this hypothesis is true, or whether the structure of high-organic-sulphur coals is

quite different from that of normal coals containing oxygen. Much of the sulphur in Rasa coal is claimed to be in ring form, probably thiophenic.

The Rasa coal, like most other coals with high-organic-sulphur contents[6,23,86], is notable for its pronounced coking ability, despite the fact that its carbon and volatile contents are indicative of a non-coking or poorly-coking coal. According to Brooks[23], this coking ability is very probably due to the presence of the organic sulphur, and is most marked when accompanied by a high hydrogen content.

In general, too,[23] high-organic-sulphur coals appear to have lower softening temperatures than low-sulphur coals of the same carbon and hydrogen contents, which could be due to the replacement of oxygen by sulphur. In simple compounds in which intermolecular hydrogen bonding can occur, this* invariably results in a reduction of melting point, and according to Brooks[23] it is possible that the main effect of sulphur in the coal structure is to lower the softening temperature by reducing the intermolecular hydrogen bonding, compared with coals of the same carbon and higher oxygen contents. Coking normally occurs only in those coals in which fusion occurs at the same or at a lower temperature than that of extensive thermal decomposition, and if sulphur has the effect of lowering this fusion temperature,

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*Electronegativity values (Pauling) for oxygen and sulphur are 3.5 and 2.5, respectively[25].

high-sulphur coals would be expected to give cokes comparable with those from coals of higher carbon and lower volatile contents.

V. The Behaviour of Coal Sulphur during Carbonisation

In the carbonisation of coal, the chemical structure is partially broken down by the application of heat, producing a solid carbonaceous residue ("coke") and volatile liquid ("tar") and gaseous ("coal gas") products. During carbonisation, the original sulphur-containing compounds are also partially broken down, about half being fixed in the coke, and most of the remainder leaving in the gas.

Decomposition of Inorganic Sulphur

The decomposition of iron pyrites[29,60] commences at about 300-350°C, with pyrrhotite (a solid solution of sulphur in ferrous sulphide (FeS) formula FeS to $FeS_{1.2}$) and sulphur vapour being formed[29,91,121,122]. The dissociation pressure reaches atmospheric at 693°C, and the reaction proceeds very rapidly at 850°C. The reaction is accelerated by the presence of carbon above about 300°C, owing to the formation of carbon disulphide[121,156]. In the presence of hydrogen, decomposition occurs at about 300°C; carbon monoxide, moist carbon dioxide, steam and ammonia also accelerate the decomposition of pyrite to lesser extents. In coals, the reaction is normally complete at about 600°C, although this temperature may be dependent upon the coal rank[91]. Most of the sulphur released by the decomposition of the pyrites is volatilised as hydrogen sulphide, the rest usually reacting with the coke to form complex organic compounds.

N.B. The method of analysis for mineral sulphides in coke may be of doubtful reliability, particularly if significant quantities of organic sulphur are present[10]. For this reason, results from the references quoted above should be treated with caution, as far as pyrrhotite contents are concerned.

Pyrrhotite melts over the range 1100 to 1190°C, with some decomposition[29].

The metallic sulphates present in coal are reduced under coking conditions to the corresponding sulphides[113]. Again, the extent of this reaction appears to be dependent upon the rank of the coal[91] and the coking temperature.

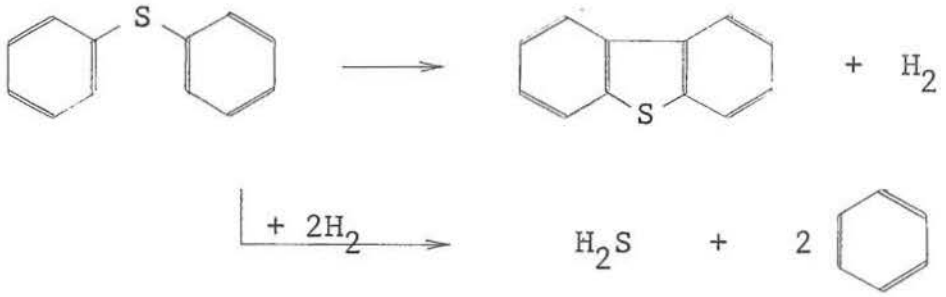
Decomposition of Organic Sulphur

Virtually nothing is known of the decomposition behaviour of organic sulphur in coal. However, a number of useful conclusions may be drawn from a consideration of the results of pyrolysis of pure organic sulphur compounds, of the type most likely to be present in coal. Much of the following discussion, on the behaviour of pure organic sulphur compounds on pyrolysis, has been abridged from the review by Given and Wyss[60] (who based their article on the publications of Hurd[76], Emmett Reid[50], and Tarbell and Harnish[143]), and on the experiments reported by Jones[81], a co-worker of Given.

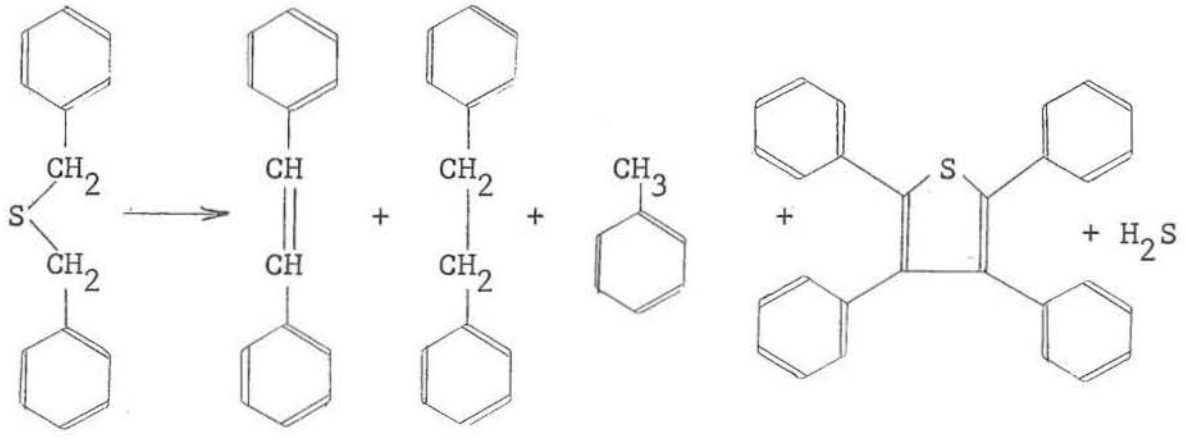
In general, when aliphatic sulphur compounds

(e.g. mercaptans, sulphides and disulphides) decompose, some sulphur is split off as the element or hydrogen sulphide, but much remains attached to the alkyl groups. The reaction usually proceeds at an appreciable rate by 500°C.

Some of these compounds include thiophene derivatives among their products of pyrolysis, e.g. the aromatic sulphides often undergo ring closure, forming complex thiophene compounds. Diphenyl sulphide gives dibenzo thiophene and benzene:



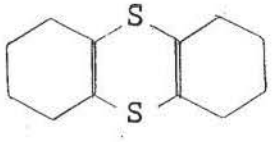
Dibenzyl sulphide yields a variety of products when heated. Decomposition is detectable at 185°C and rapid at 262°C. The products include (a) stilbene, (b) dibenzyl, (c) toluene, (d) tetraphenyl thiophene, and hydrogen sulphide.



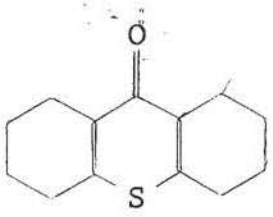
(a) (b) (c) (d)

The thiophene ring system approaches benzene[12] in thermal stability and, like benzene, when reaction does occur, gives a fair proportion of more highly condensed or otherwise stable structures in which the original ring system remains intact. Jones[81] pyrolysed dibenzothiophene at 800°C, and found that benzene was the major product, together with a thermally stable char which contained virtually all the sulphur. He concluded that sulphur bound in thiophene linkages is not released during carbonisation, and also is not a source of thiophene in the coal tar distillate.

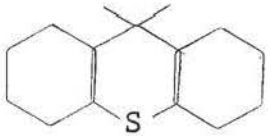
Jones also pyrolysed the six-membered ring compounds thianthrene (a), thioxanthone (b), and thioxanthene (c).



(a)



(b)



(c)

Thianthrene yielded benzene, hydrogen sulphide, carbon disulphide and thiophene, together with a char containing sulphur and carbon in a thermally stable complex. Thioxanthone and thioxanthene were both completely decomposed at 800°C, with all of the sulphur volatilised as sulphur dioxide and hydrogen sulphide, respectively. Jones pointed out that, although these structures are not thermally stable, they provide a source of reactive sulphur

for reaction with incandescent coke; he also noted that the pyrolysis of all of these heterocyclic sulphur compounds resulted in products normally found in the coal tar distillate.

It seems, therefore, that on purely thermal treatment of organic sulphur compounds, the sulphur is not all eliminated, a large proportion often being fixed in a carbonaceous residue, either as a carbon-sulphur complex, or incorporated within highly stable and highly condensed aromatic systems, possibly as thiophene rings. Thus, if the comparison is valid, it might be expected that some sulphur would always remain in the coke after organic sulphur-containing coal is carbonised.

This view has been confirmed by all the experiments that have been reported in the literature; it is not possible, by purely thermal treatment (up to about 1200-1300°C), to remove more than at most about half of the sulphur originally present in the coal. The reason is, almost certainly, that when coals are heated some of the sulphur is converted to a more stable form, and that this reaction competes with the process of sulphur volatilisation. According to Trifonov[146], the organic sulphur fixation process is virtually complete at about 600°C.

Organic Sulphur in Coke

Knowledge of the chemical structure and behaviour of the organic sulphur compounds in coke is of a very

rudimentary nature, and is insufficient for a consideration of their possible role in any desulphurisation process.

According to reference 7, the available information indicates three possible structures for the carbon-sulphur complexes in coke, in addition to the pyrolysis products discussed above:

(a) Capillary condensation within the micropores of the carbon, as the element or as simple derivatives such as hydrogen sulphide or carbon disulphide. It is unlikely that significant quantities of sulphur are present in this form, since neither high-temperature treatment nor solvent extraction is capable of removing other than very small quantities of sulphur from coke.

(b) Incorporation of the sulphur in solid solution, or as part of the lattice structure of the carbon. No evidence is available to support this theory.

(c) Retention of the sulphur on the internal surface of the carbon, as chemisorbed surface sulphides. Evidence[7] for this theory has come from the use of electron spin resonance to examine the formation and thermal stability of surface sulphides accompanying the interaction of specially prepared carbons with sulphur vapour and with hydrogen sulphide, under various reaction conditions. Tentative conclusions were "that surface sulphides made an important contribution to the organic sulphur content of coke; that their structure is essentially one involving bonding of

sulphur at the edges of graphitic layers of carbon; and that dehydrogenation by sulphur and the interaction of sulphur with free radicals present in the coke or semicoke contribute to the formation of the complexes during the carbonisation of coal. Small crystallite size of the coke and the presence of defects of various kinds in the crystallite structure, as well as differences in accessibility, would be expected to influence the retention of sulphur during carbonisation."

Groups possibly present as surface sulphides include $\begin{matrix} C \\ C \end{matrix}\!\!>\!\!S$, C-SH, C = S, and thiophene rings. According to reference 7, it is not improbable that the sulphur-carbon complexes formed by surface reactions, and by pyrolysis of sulphur compounds are essentially similar, and that in both the sulphur may be present in combination at the edges of the graphitic layers of the carbon, as thiophene residues or as sulphide linkages.

As reported by Theissen[69] and Howard[144], the distribution of the coal sulphur between solid and gaseous products has been the focus of considerable study over the past 45 years, the object being to determine the conditions under which the greatest possible amount of sulphur is volatilised during carbonisation.

Most of the work done has involved empirical experimentation on a wide variety of coals, in both laboratory and full-scale equipment. Because of the wide variations found

in the properties of coals from different areas, one would not expect the results to be either comparable or suitable for general application. However, after correlating the results for 443 cokes, prepared at carbonising temperatures from 500 to 1100°C and ranging from 0.47% to 4.00% sulphur in the cokes, Lowry, Landau and Naugle[97] found that the percentage sulphur in the dry, ash-free coke (S_c) could be expressed in terms of the percentages of organic (S_o) and pyritic (S_p) sulphur in the dry, ash-free coal, by the expression:

$$S_c = 0.85\ S_o + 0.86\ S_p$$

After summarising the work of various experimenters, Theissen[144] determined the similar relationship:

$$S_c = 0.45\ S_o + 0.62\ S_p$$

It appears, then, that the sulphur from both organic and inorganic sources is partitioned on the average in a similar manner between solid and gaseous products. Some confirmation of this view has been obtained from experiments in which radioactive S^{35} was used to follow the reactions of pyritic sulphur content of coals[26,43,44], but these conclusions have been disputed by other workers[59,91,141] who find them to be true only for lower-rank coals. What statistical analysis has been done[97] has not covered a very wide range of coal types, relative to the total variation found over the earth's surface, and the trends observed have not been found to hold for coals high in organic sulphur and

low in pyritic sulphur[40]. It is important to note, too, that the experiments[97] upon which the statistical analysis of Lowry et al was based were made on coals of roughly comparable pyritic and organic sulphur contents, carbonised in the U.S. Bureau of Mines - American Gas Association laboratory carbonisation assay test equipment. As shown by Theissen, other types of equipment give different correlating equations.

VI. Production of Low-Sulphur Coke from High-Sulphur Coal

It is the purpose of this work to investigate the possibility of producing low-sulphur coke from high-sulphur coal. To this end, it is relevant to examine some of the variables likely to be encountered, both in the coal itself and in the coking process, and their effect on the sulphur composition of the resulting coke.

Variables Affecting the Carbonisation Process

The Gaseous Atmosphere Surrounding the Charge During Carbonisation

This appears to have a very great influence upon the relative proportions of sulphur volatilised and fixed in the coke. Gases used[22,69,144] include direct steam, steam generated from moisture within the coking charge, steam and air mixtures, steam with nitrogen, hydrogen, chlorine and oil gas; carbon dioxide, nitrogen, hydrogen, carbon monoxide, water gas, hydrogen chloride, illuminating gas, anhydrous ammonia, methane, ethylene, natural gas, air and oxygen. None of these treatments has been found to be economical when applied to full-scale plant.

Neutral gases, such as nitrogen, appear to have little effect; it is unlikely that they take any part in the process other than dilution of the gaseous reaction products as they are formed.

Oxidising gases, such as air and air-steam mixtures,

result in appreciable desulphurisation, but at the expense of heavy losses of coke due to combustion, and substantial deterioration in coke quality.

Reducing gases, such as hydrogen and ammonia, which convert the sulphur compounds in the coal or coke to hydrogen sulphide, appear to be the most generally effective. Zielke et al[161] used hydrogen/steam mixtures to study the desulphurisation of chars in an experimental fluid bed, and found that pure hydrogen was much more effective, in terms of desulphurisation at a given percentage carbon gasification. Fig. 3(a) shows that, for one particular char, in pure hydrogen, the sulphur content was a unique function of the percentage gasification of carbon, and was independent of pressure. It was also shown that by using a 15% methane/85% hydrogen fluidising gas, desulphurisation could be achieved without loss of carbon.

The Sulphur Content of the Gaseous Atmosphere

It is well-known that carbonaceous materials such as coke are capable of reacting with hydrogen sulphide, and that the reaction is reversible[70,71,72,120,121,122,123]. The reaction appears to involve the formation of carbon-sulphur complexes[7,55,59,70,118,120,142], with sulphur in solid solution, with sulphur atoms replacing carbon atoms in the graphite lattice, or with formation of chemisorbed surface sulphides; in each case resulting in a stable

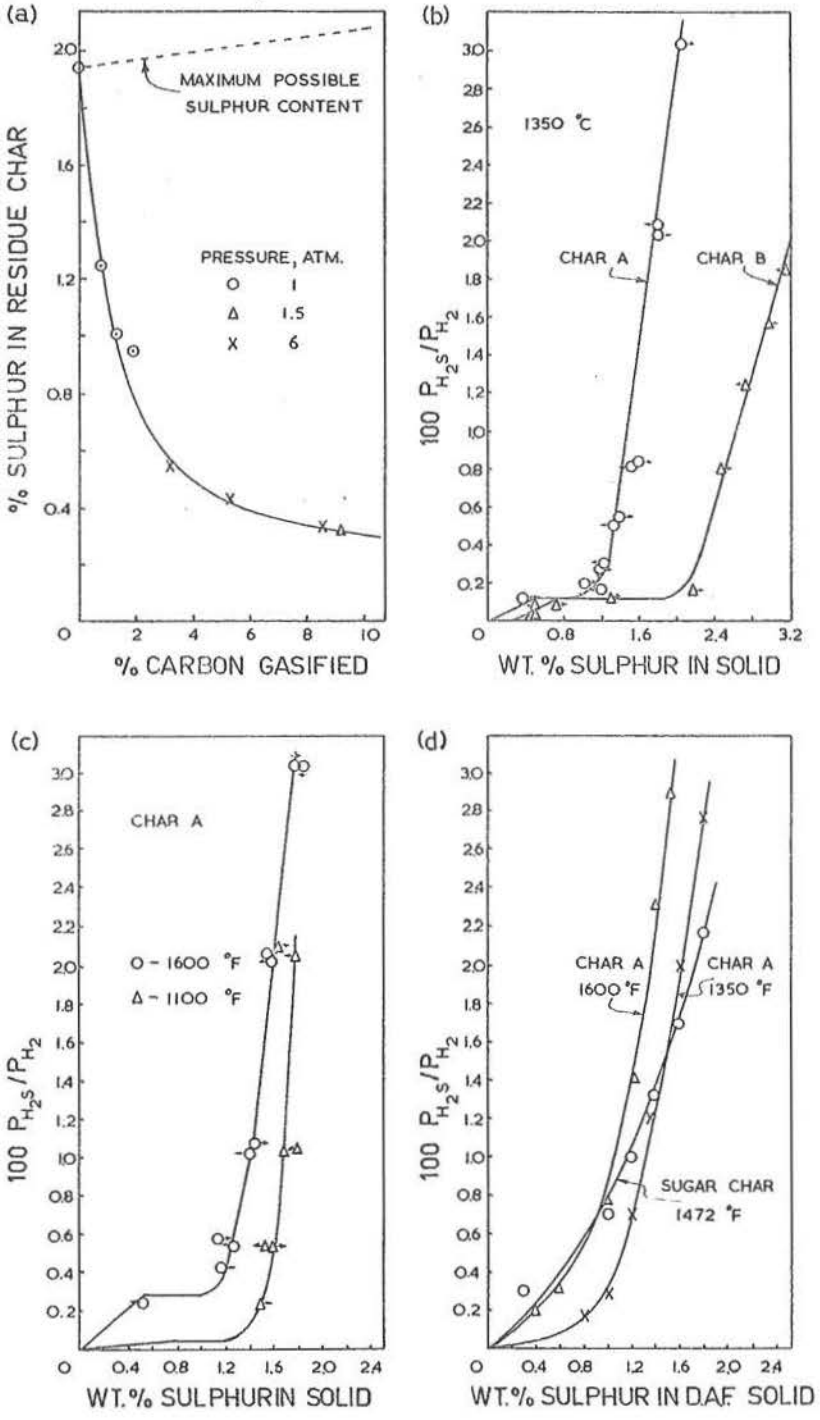


FIGURE 3 (a) DESULPHURISATION WITH PURE HYDROGEN (ZIELKE ET AL[161])
(b),(c) and (d) TOTAL INHIBITION ISOTHERMS (BATCHELOR ET AL[16])

but undesirable structure. From experiments involving the direct reaction of sulphur with coal, it has been suggested that the fixation of sulphur can be attributed to dehydrogenation of hydroaromatic structures in the organic matrix[103], or to dehydrogenation and cross-linking of aromatic nuclei[79,88]. If coal is carbonised after heating with sulphur at 300-350°C, the yield of volatile matter is drastically reduced and the coke has an increased sulphur content[79]. Sulphur can also be physically adsorbed on to the coke surface, but in this case is relatively easily removed upon treatment with hydrogen at elevated temperatures. It appears, however, that these are not true equilibrium processes, because the results depend upon the thermal history and origin of the carbonaceous material.

As a continuation of the work of Zielke et al, Batchelor et al[16] obtained equilibrium and rate data for the desulphurisation in a fluidised bed at 700-900°C, of a number of low-temperature chars, using hydrogen-hydrogen sulphide mixtures of various concentrations. It was found that, using gas of a given concentration, low-sulphur chars took up sulphur, and high-sulphur chars lost sulphur, in approaching their respective equilibrium compositions. The sulphur content corresponding to total inhibition could thus be bracketed by approaching it from both sides. Figs 3(b),(c) and (d) give typical total inhibition curves and show that the equilibria are dependent upon both the type of char used and the temperature at which the process

is carried out. The plateaux in Figs 3(b) and (c) correspond to the equilibrium in the reduction of ferrous sulphide, $FeS + H_2 = H_2S + Fe$. (All pyrite from the original coal had apparently been reduced to ferrous sulphide, during the char pretreatment stages.) From Fig. 3(d) the total inhibition for the organic sulphur content, like that of the sulphide sulphur, becomes more marked as the temperature is lowered. Fig. 3(d) also shows that the nature and prior history of the char has a considerable effect on the isotherm.

From a relatively small amount of data on the rate of the process, the authors concluded that, for this system, the kinetics of sulphur elimination were roughly first order. As has been shown by the results of a number of workers (summarised by Squires[138]), the gasification of carbon by hydrogen is a first-order reaction, but the carbon reactivity is strongly dependent upon the previous thermal and environmental history of the carbon. It would appear, then, that the reactions of coal sulphur with hydrogen may be of a similar type.

According to Volovik[147] who investigated cokes from three by-product coking plants in the Ukraine, there is a non-uniformity in the distribution of sulphur in the coke mass. Volovik states[117] that the sulphur content in the coke "cake" rises from the axial part of the oven towards the heating walls, i.e. in the direction of gas movement

in the coal charge during coking, the difference in sulphur content being over 20%. This result implies a mechanism, as reported by Pokhvisnev et al,[117] whereby the gas generated at a later stage in the process, in passing through the surrounding layers of hot coke, reacts with this coke, thereby increasing its sulphur content. Such a mechanism had been previously suggested by Batchelor et al[16].

The Presence of Mineral Matter

At higher temperatures, it appears that the distinction between inorganic and organic sulphur becomes blurred; some of the sulphur released by the pyrites may, as discussed earlier, combine with the coke and form organic sulphur, while sulphur compounds deriving from the organic material can be taken up by the mineral matter. It has been shown that, in particular, calcium carbonate, iron oxide[26], calcium sulphate[104] and coal ash constituents[17] prevent volatilisation of organic sulphur, converting it to inorganic forms.

This behaviour was not appreciated until relatively recently, when radioactive tracer techniques were used. For this reason many conclusions reached in earlier experiments reported in the literature cannot be considered reliable due to the (implicit) assumption that the sulphur in the coke was combined in the same general manner (i.e. organic or mineral) as in the original coal.

According to Černič-Simić[26], the effect is not observed in coals in which most of the sulphur is present in organic form, particularly if there is a low ash content, since in such cases there is not sufficient mineral matter present to fix a significant proportion of the sulphur released.

Volatile Evolution

Although relatively little attention has been paid to the influence of this factor, it is claimed[3,26] that the greater the volatile content of a coal, the lower is the sulphur content of the coke.

As has been discussed earlier, it appears that the ratio aliphatic/aromatic sulphur is greatest in high-volatile coals, and for this reason, taking into account the known lower thermal stability of thioethers relative to ring compounds[3,60], it might be expected that these coals would experience a greater loss of sulphur during carbonisation than coals of lower volatile content. No evidence is available to support this suggestion.

It is also interesting to note that, according to Angelova and Syskov[3], who coked pyridine extracts of coals (to exclude the influence of inorganic compounds of sulphur), the percentage volatilisation of organic sulphur compounds is always higher (by 8-13%) than the percentage loss of total volatiles from the coal. (This was observed in coals

in which only 5-10% of the organic sulphur was present as thioethers (the remainder, by inference, being in ring form), and is almost certainly the result of a significant degree of decomposition of the aromatically bound sulphur.)

The results of Angelova and Syskov are supported by the data of Goswami and Roy[61] for Baragolai coal (Assam), and Marshall and Draycott[100] for Tangorin coal (Australia).

Table 3

Sulphur and volatiles losses
at different coking temperatures

Goswami and Roy			Marshall and Draycott		
Temp. °C	% loss of sulphur	% loss of volatiles	Temp. °C	% loss of sulphur	% loss of volatiles
500	50	46.9	420	2.4	2.41
600	51	48.0	520	33.26	40.3
700	54.5	46.9	620	54	41.11
750	55.3	46.9	700	57	44.54
800	61	47.0	800	58.2	47.17
850	63	47.5	920	61	50.03
900	63.5	48			
950	63.8	48			

(Coal properties: Baragolai, total sulphur 4.57%, organic sulphur 3.99%, volatile matter 46.1%, moisture 3.33%, and ash 2.42% (air dry basis).
Tangorin, total sulphur 5.8%, organic sulphur 5.45%, volatile matter 54.2% (d.a.f. basis).)

At temperatures above 600°C, the percentage loss of sulphur is greater than the percentage loss of total volatiles. It is also interesting to note that, above 500°C, the emission of total volatiles is close to completion, whereas sulphur loss continues steadily, up to the highest temperatures used. This behaviour is quite unexpected, since if one accepts the generally-held view that organic sulphur is an integral part of the coal "molecule", it is to be expected that sulphur compounds would be given off at the same time and at the same rate as total volatile matter. One possible explanation is that the sulphur-containing parts of the coal molecule decompose more slowly than the other parts, probably via intermediate compounds of greater thermal stability, which are not decomposed until higher temperatures are reached.

Insufficient data are available to determine whether the differences in coking behaviour of the two coals are due to the coals themselves, or to the types of coking process used by the authors.

Rate of Heating

An increase in the rate of carbonisation of a number of British coals caused a small reduction in the percentage retention of sulphur by the coke[8].

In the opinion of the writer, it is also possible that the rate of heating influences the process of re-absorption

of sulphur on to the coke, because quick heating results in more rapid emission of volatile products, which would tend to flush sulphur compounds away from the coke surface before they had time to be absorbed. This view is at least partially supported by the experiments of Chukhanov et al[32] (discussed in detail later) in which coal was heated extremely rapidly and then allowed to decompose isothermally. The extent of desulphurisation appeared to be greater than that for "conventional" coking processes at all temperatures above about 500°C, even for decomposition times as short as 0.35 seconds. Similar experiments by Kaliuzhnyi[82] on the behaviour of forms of sulphur in a shale, subjected to this very rapid pyrolysis, indicated that the evolution of organic sulphur proceeds to a considerable extent at temperatures above 350°C for a decomposition time of 5 minutes. An important aspect of these experiments is that, during the initial stages of coking, the particles of coal or shale were falling freely through a stream of fresh nitrogen, and the consequent rapid flushing away of the volatile products (including volatilsed sulphur) would prevent re-absorption of sulphur by the hot coke.

Chukhanov et al have also shown that there is a very great difference in yield and composition of the various volatile products, between slow and rapid heating; this result has been confirmed by Loison and Chauvin[95] and by

Peters and Bertling[115], both of whom independently studied rapid coking in types of equipment quite different from that of the Russian workers. The effects of rapid coking on the composition of the coke were not reported in detail, but it was implied that an appreciable effect was observed.

Another effect that may be related to the rate of heating is the connection between volatile evolution and sulphur content, discussed above. A number of experiments (considered in more detail later in this survey) involving rapid heating of coal[49,79,95,115,160] have shown that the volatile matter evolution on rapid heating is greater than that determined according to the B.S. test, in some cases an increase of as much as 50% being observed. Therefore, if sulphur loss can be assumed to be related to volatile emission, it is to be expected that a change in the rate of heating will affect the sulphur content of the coke.

It is not known which of these effects - volatile evolution, sulphur reabsorption or product distribution - has the greatest influence as far as the effect of rate of heating on residual sulphur content is concerned.

Coal Rank

It is claimed by a number of workers[26,59,91,141] that the retention of sulphur in the coke (both organic and total) is a function of rank, low rank coals liberating appreciably larger proportions of sulphur than high rank

coals. However, the available data show a wide spread, and according to Černič-Simić[26] it is probable that the effect of rank is closely bound up with that of volatile content. Nevertheless, the ratio aliphatic/aromatic sulphur appears to be much lower in high rank coals, and the different decomposition behaviour of these two classes of compound could therefore affect the residual sulphur in cokes made from coals of different rank.

Temperature and Pressure

The sulphur content of coke apparently decreases with increase in carbonisation temperature[26,56,57,61,100]; this is to be expected, in that harsher conditions are more likely to cause thermal breakdown of sulphur compounds, and desorption of adsorbed sulphur.

According to Davis et al[38]; in the gas from low-temperature carbonisation, mercaptans are dominant, and carbon disulphide almost absent, whereas in the gas from high-temperature carbonisation the reverse is true; some carbon oxysulphide is also present in some cases. As Fuchs[55] has shown by thermodynamic analysis, at 900°C aliphatic sulphur compounds in the gas phase are decomposed, and only hydrogen sulphide, carbon disulphide and carbon oxysulphide are stable.

It is claimed that the effect of low pressure during carbonisation is that sulphur retention tends to increase, particularly at high temperatures[11,144], whereas high

pressure reduces the temperature at which changes occur during carbonisation[134], i.e. at any given temperature, an increase in pressure causes a reduction in the sulphur content of the coke. In the opinion of the writer, it is unlikely that this is due to high pressure influencing the reactions of volatile sulphur with coke, since the opposite effect would be expected from thermodynamic considerations. However, high pressure would favour such reactions as hydrogenation of coke sulphur, and so it is possible that some such effect may have been present, particularly at temperatures at which hydrogen evolution proceeds rapidly.

Particle Size

When carbonising coal in laboratory-scale equipment in the presence of hydrogen, it has been observed[117] that a very great increase in desulphurisation occurs for particles smaller than 0.2 mm, compared with particles larger than about 1 mm, for the same period of treatment. However, it is highly probable that this is due to more rapid reaction of hydrogen with sulphur in the coke, rather than with coal sulphur compounds during the coking process; evolution of gases from the coal would reduce counter-diffusion of the hydrogen until the main process of gasification was complete.

Presence of Solid Additives

Theissen[144] and Howard[69] have summarised the results of a great many experiments, reported in the literature, in which various solid chemicals were added to the coal charge before or after carbonisation, with the intention of increasing the volatility of the sulphur in the coal, or else of preferentially combining with the sulphur. In the latter case, the combined form would be harmless, as far as the end use of the coke was concerned, or be in a form that could easily be leached out, thereby removing the sulphur in its compound form with the additive. In some cases, this treatment was combined with the use of various gases during carbonisation.

Additives used include[5,22,33,37,51,59,61,69,81,84,91,96,105,106,126,144] dry or hydrated lime, calcium, magnesium, manganese, iron, and aluminium oxides; sodium, calcium, and magnesium carbonates; magnesium and silicon dioxides; calcium, iron and magnesium phosphates; calcium orthosilicate, Portland cement, caustic soda; ammonium, calcium, sodium, magnesium, zinc and tin chlorides; pure iron, iron ore, metallic catalysts (magnesium, chromium, copper, calcium and lead compounds), potassium chlorate, calcium hydride, ferrous sulphide, sodium bicarbonate, sodium aluminate, alkaline cyanide, dolomite, sodium borohydride and pyromellitic dianhydride.

In many instances, the treatments outlined above have

been very successful from the point of view of desulphurisation of the coke, but other disadvantages - notably the effect on other aspects of coke quality and the cost of the treatment - have prevented practical implementation of the experimental findings.

Desulphurisation of High-Organic-Sulphur Coals

Taking into account the chemistry of organic sulphur compounds of the types considered above, reduction with hydrogen seems to be the most promising avenue of investigation into the problem of desulphurising high-organic-sulphur coals, from both theoretical and practical viewpoints. Oxidation would not be so effective, since conditions sufficient to oxidise the sulphur compounds cause serious coke losses by combustion. The use of solid or liquid additives does not seem promising either, due to the complexity and cost of these methods and the doubtful quality of the end product.

It also appears that rapid heating may have an appreciable effect on the composition of the coke produced; this factor is worth investigating. It is also important that mass transfer conditions during carbonisation are such as to ensure removal of volatile products before they have the opportunity to react with the hot coke.

VII. Kinetics of Carbonisation Processes Suitable for Maximum Desulphurisation of Coal

From the preceding sections, it will be apparent that in order to study the decomposition of organic sulphur in coal, certain precautions must be taken to reduce the number of variables influencing the results.

Firstly, the gaseous atmosphere surrounding the coal particles must be free from carbonisation products, especially sulphur compounds. This will ensure that reabsorption on to the coke is small, and means that individual coal particles must be coked in clean gas, in relative isolation from other particles, to minimise mutual interference.

Secondly, apart from the previously mentioned advantages of rapid heating, it is desirable that the carbonisation be carried out under isothermal conditions, so that the mechanism of decomposition may be more easily studied at different coking temperatures. The coal particle must therefore be sufficiently small for heat conduction within the particle to be rapid, and coking conditions must be such that the rate of radiation and/or convection heat transfer at the surface of the particle is as high as possible.

Only two techniques seem capable of satisfying the requirements listed above: fluidised bed and disperse phase carbonisation (shown schematically in Fig. 4).

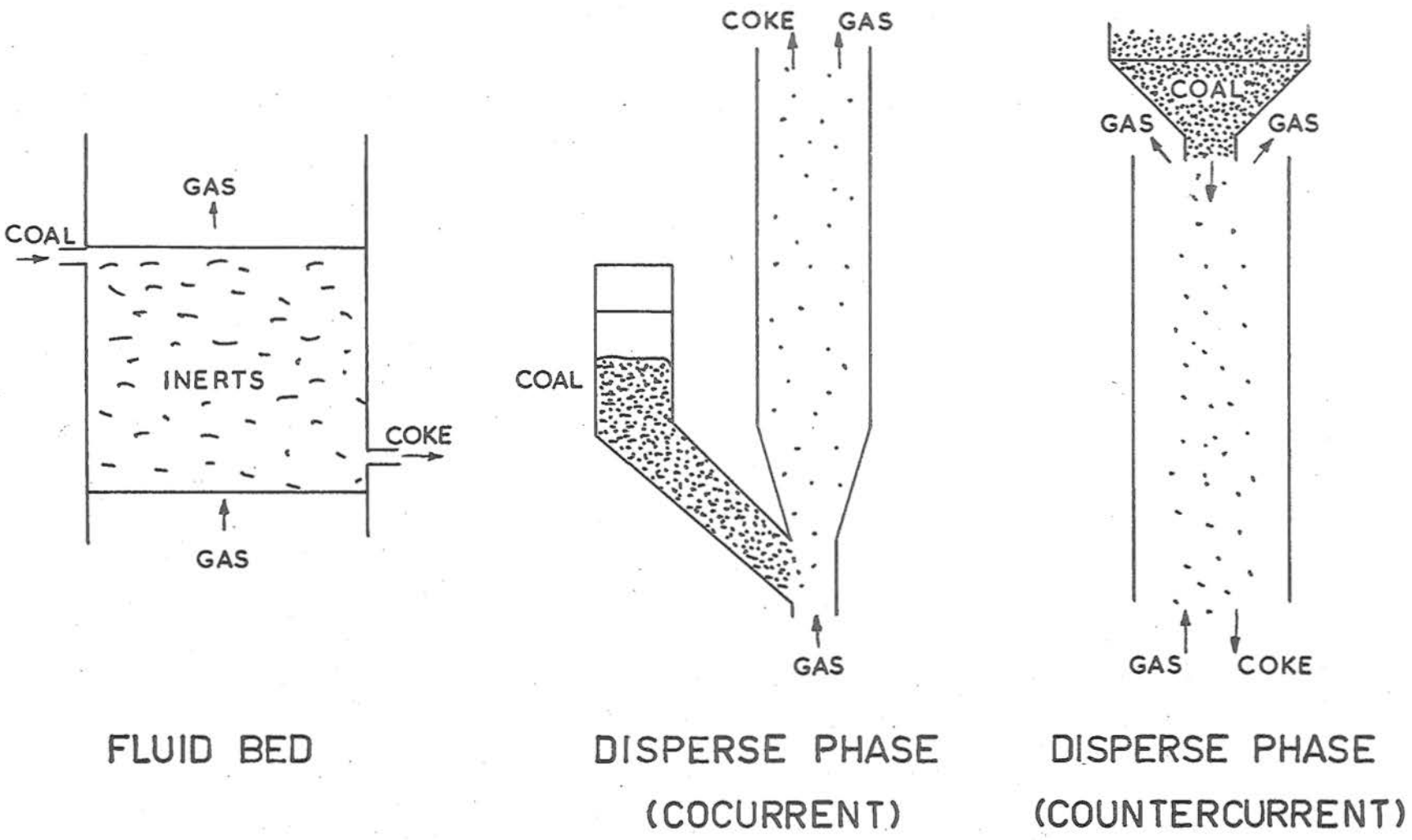


FIGURE 4 PROCESSES FOR RAPID CARBONISATION OF COAL.

In disperse phase carbonisation the coal, in the form of a fine stream or cloud of particles, is entrained in a gas and passed through a heated tube, or allowed to fall freely through a stream of gas in a vertically-mounted heated tube. In the former case the coal/gas flows are cocurrent, and in the latter case usually countercurrent. The tube may be heated externally, or internally by the use of heated gas or by partial combustion of the coal. It is claimed[160] that heating rates of the order of 10^7 °C/min. can be achieved in disperse phase carbonisation.

The best way of ensuring rapid heating of the coal in a fluid bed is to inject small quantities of fine coal into a preheated bed of some inert solid such as sand[114,116,139]. The inert solid acts as a heat carrier and, with the known high heat transfer characteristics of fluidised beds, the coal particles rapidly reach the temperature of the bed. The inert material should be present in considerable excess for two reasons: the endothermic heat demand of the coal would otherwise lower the temperature of the bed appreciably; and the dilution of the coal by the inert solid reduces the effects of interference from the carbonisation products of other coal particles. The fluid bed also has the advantage that carbonisation products are rapidly flushed away by the incoming fluidising gas.

Various combinations of fluid bed and disperse-phase methods have been used for char and gas production in the U.S.A. (U.S. Bureau of Mines[9]) and Australia (C.S.I.R.O.[150] and B.H.P.[111,133]).

Since these two techniques have been used in a number of studies of the kinetics of volatile evolution from coals under isothermal conditions, a discussion of the results of the investigations would not be out of place in this survey. (Some of the information in the following sections was obtained from the reviews by Jones[80] and Yellow[160].)

Disperse Phase Carbonisation

The disperse phase system of carbonisation was patented in the U.K. in 1913[93] and 1918[157], and used in the U.S.A. for the commercial-scale production of low-temperature coke in the 1920's.[85,125,137] More recently, the method has been used in pilot-scale retorting of shale[21] and in various forms for gas and char production in the U.S.S.R.[32,110], U.S.A.[9], Australia[111,133,150] and U.K.[34].

The behaviour of coal particles subjected to this type of treatment was first studied by Sinnatt et al in 1922[109,131]. Their observations[125] included measurements of the volatile content and coking ability of the product at different temperatures, and a detailed microscopical examination of the coked particles, which were hollow globules, termed cenospheres.

The first detailed fundamental study of the kinetics and mechanism of coal decomposition, using this technique, was carried out by Russian workers under the general direction of Chukhanov[14].

Theoretical work by Chukhanov[30,31] has shown that coal particles smaller than 100 microns can be heated by hot gas to 95% of the temperature of the gas, within 0.1 sec, and those of 20 microns within 0.004 sec. His analysis does not include effects due to radiation from the walls of the vessel, the insulating effect of the envelope of the particle's own distillation products, or the effects when concentrations of particles are sufficiently high for those at the centre of a cloud to be subject to conditions radically different from those at the outside of the cloud. The endothermic heat demand of the carbonising coal was also ignored.

The first experiments[14,31,130] carried out by Chukhanov and co-workers involved dropping samples of Moscow-district and Cheremkhovo fine coals down a heated tube, through a gentle countercurrent stream of nitrogen. Longer residence times were obtained by collecting the coke in a small cup within the furnace, and tipping the contents out into a water spray after the required decomposition time. After drying and weighing, the coke was analysed for volatile matter, and the volatiles released obtained by difference. (The authors do not

investigate the assumption, implicit in their work and mentioned explicitly in their later papers[32], that the maximum volatile evolution in the rapid heating process is the same as that measured by heating slowly in the standard test methods. They also ignore any effects resulting from the rapid quenching of hot coke by cold water.)

It was found that that the rate of devolatilisation was extremely rapid during the first 0.5 second of carbonisation, and continued much more slowly for the next three minutes, after which the evolution of gas virtually stopped.

In order to study the behaviour of the coal during the initial stages of carbonisation, a more elaborate experimental technique was developed, in which small coal particles (0-74 microns) were entrained in a stream of superheated steam and carbonised for short periods before quenching in a water spray. It was found that there was an extremely rapid loss of volatile matter during the first 0.1 second followed by a slower (by a factor of about 10) but still appreciable loss between 0.1 and 0.5 second. (The authors did not take account of possible effects of the superheated steam on the carbonisation process. In the writer's opinion, it is not inconceivable that such an effect may have been present, although its influence might well be minor, especially during the early

stages when an envelope of volatile carbonisation products still surrounds and insulates the particle.) Typical data for decomposition were: 75% of volatiles generated in 30 seconds, and 90% within 5 minutes.

On the basis of the results obtained, Chukhanov et al divided the process of thermal decomposition under rapid heating conditions into three main stages:

Stage 1 - Extremely rapid carbonisation during the first 0.1 second, characterised by the high content in the volatile products up to 450-550°C) of oxygen-containing gases, such as H_2O, CO_2 and CO. The yield of volatile products during this period is usually higher, the greater the content of oxygen in the coal. Sulphur compounds[77] are not given off until temperatures of about 500°C are reached, and then only in small amounts; tarry products also do not appear before this temperature. This stage is closely connected with the heating of the coal and may be bound up with the release of absorbed or adsorbed water.

The initial stage can be broken down into two further stages: the first of duration 0-0.06 second ("activation energy"*about 7 Kcal/mole), and the second of up to 0.1 second ("activation energy" 9 Kcal/mole). Even so, several reactions are in fact proceeding simultaneously, and values of rate constants and activation energies are

*Footnote on p.45.

therefore averaged over the assumed first-order decomposition reaction.

Stage 2 - Principal thermal decomposition, at a relatively much slower rate, proceeding for 2-3 minutes ("activation energy" 6.3 Kcal/mole), the main products being the valuable gaseous hydrocarbons and tars. Organic sulphur compounds[77] are liberated during this stage.

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*Yellow[160] has pointed out that unless the mechanism of the reaction is known, activation energies derived from experimental rate constants, even for simple solid-state reactions, may be seriously in error. Since the mechanisms of the reactions involved in the pyrolysis of coal are completely unknown, all "activation energies" quoted for this process are dubious and empirical. Additional uncertainties arise from possible transitions between chemical and physical rate control as particle size, temperature and heating rate change, and the many possible ways of defining the extent of reaction and amounts of reacting material. Provided the broad reaction scheme assumed is similar in each case, however, experiments under the same conditions should give rise to comparable apparent activation energies; while providing a useful way of empirically describing the temperature-dependence of the devolatilisation reaction, relatively little chemical or physical significance can safely be drawn from the results.

Stage 3 - Degassing of the coke, proceeding at a very slow rate for up to several hours, during which mainly methane and hydrogen are released. About 15-20% of the total volatile matter is given off in this stage.

The smallness of the "activation energies" probably implies that the decomposition is controlled by physical rather than chemical processes. It is claimed by Yellow[160], however, that subdivision of the decomposition curves into a set of reactions with definite activation energies assigned is not justified.

It is possible that the third stage is at least partly related to the release of gases adsorbed or absorbed while the coke is in a stagnant film of its own carbonisation products. This may be a result of the layout of Chukhanov's apparatus, in which the coal, after primary heating, drops into a cup in the lower part of the furnace to be retained at constant temperature until quenched. Partial support for this hypothesis is provided by Stone et al[139] (see later) who suggest that the low activation energy for the third stage indicates that the process is controlled by some physical factor such as pore diffusion.

From a kinetic analysis of the results of the experiments, Chukhanov has postulated that the decomposition of coal proceeds as a number of complex series and parallel independent reactions, each of the first order,

but having different activation energies and rate constants. His results, confirmed in essence by other workers (discussed later), conclusively disprove the theory of van Krevelen et al[28,87,89,90] which considers the decomposition of coal to proceed as three simple consecutive reactions. If this theory of pure consecutive reactions were correct, then no change in carbonisation conditions (in particular, the rate of heating) would affect the final product distribution at any particular temperature. The experiments of Chukhanov[14,32] have shown a very considerable effect of disproportionality between the yield and nature of the products obtained at high and low heating rates, thus showing that at least some of the decomposition reactions occur in parallel, and not in series. However, it should be noted that the theory of van Krevelen et al was developed purely as a mathematical model to describe some of the phenomena occurring during the heating of coking coals; its authors are aware that their model is a considerable over-simplification of the "true" process.

Unpublished work by B.C.U.R.A. on the devolatilisation rates of rapidly-heated fine coal (reported by Yellow[160]) indicates that the rapid initial loss of volatiles can only be accounted for by rate-controlling processes of a physical, rather than chemical (i.e. bond breakage) nature. Yellow suggests that the initial stages of decomposition of coal involve a series of simultaneous reactions and

physical processes, in which the products formed may be (a) fragments of coal substance carried away by escaping gases, (b) large molecules evaporated from the coal surface, or (c) small molecules that rapidly polymerise, or by a combination of all three of these mechanisms.

Mechanism (a) is supported by examination of the volatile solids (no liquid tars were detected) produced by rapid heating of small coal particles at temperatures up to 900°C. Infrared absorption analysis showed that the composition of these solids was very similar to that of the original coal, but contained slightly less non-aromatic material. According to Yellow, "These results would be expected if fragments, perhaps of molecular size, of the coal particles were ejected into the hot gas stream in which the particles were dispersed, and there decomposed by a chemically-rate-controlled reaction, losing some of the aliphatic groups or alicyclic hydrogen."

According to any of these mechanisms, it is probable that with longer residence times further reactions would occur, in which the volatile products were cracked or polymerised, in both cases giving rise to gaseous, and probably liquid and solid products. Eddinger et al[46], in experiments similar to those reported by Yellow, report that at temperatures above 1300°C significant quantities of carbon are produced (in addition to char), showing that

volatile hydrocarbons are cracked in the vapour phase to form solid products. In one experiment at 1300°C, the solid product contained 16.2% of vapour-cracked carbon.

Yellow has stated that the difference in solids yield between rapid and slow (packed bed) carbonisation can be explained,in terms of the above mechanisms, by postulating that escape of the primary volatile products cannot occur before they react in some way to produce largely involatile products, together with small amounts of gases by chemical processes (e.g. bond breakage and dissociation). It is these secondary processes that appear as the "initial" reactions, in studies of the kinetics of devolatilisation involving slow heating in packed beds, thereby explaining the relatively high "activation energies" (of the order of 45-60 kcal/mole, for bituminous coals) found by such workers as van Krevelen et al[89].

Fluidised Carbonisation

The kinetics of volatile evolution from coal in a fluidised bed were first investigated by Stone et al[139] in 1954. These workers injected fine coal into a fluid bed of sand, and withdrew samples of the product at regular intervals for determination of volatile content. Their results are consistent with the theory of Chukhanov, namely that the evolution of volatiles proceeds in essentially three stages. "Activation energies" obtained for the three first-order consecutive reactions differed

substantially from those obtained by Chukhanov[14], being 26.2, 23.4 and 6.7 Kcal/mole, respectively. However, it is not possible to compare the two sets of results because of the differences in interpretation of the duration of the first and second stages of decomposition. It is also important to note that there was an uncertainty of at least 50°C in the bed temperature during the first 100 seconds after introduction of the coal sample, yet it was within this period that the main kinetic data were obtained. The arbitrary division of the decomposition curve into three stages may therefore be incorrect, and the "activation energies" unreliable.

A different approach was made by Pitt[116] in interpreting results obtained from experiments in equipment similar to that of Stone et al, but modified to ensure that final temperatures were reached much more quickly, i.e. in the first 10 seconds, compared with about 5 minutes in Stone's apparatus. Pitt made no attempt to resolve the experimental curve into a limited number of first-order reactions, but found that the data fitted satisfactorily an empirical equation of the form

$$\frac{V_t}{V_o} = A - B\log t,$$

where V_t/V_o is the fraction of volatile material in the char after a time t. This form of equation does not correspond to a single first-order reaction, but is characteristic of a system comprising a large number of

independent first-order reactions, covering a wide range of activation energies. The physical significance of Pitt's theory, as described by Jones[80], is as follows: "At any particular temperature, those reactions with low activation energy are responsible for the very rapid loss of volatile matter which occurs initially. Those reactions with moderate activation energies give rise to the slow loss of volatile matter following the initial rapid loss. Finally there are reactions with activation energies so high that their rate is negligible at a particular temperature. When a higher temperature is used, however, some reactions with moderate activation energies will become fast and contribute to the initial rapid fall of volatile matter. Moreover those reactions with high activation energies will then proceed at a measurable rate and contribute to the slow loss of volatile matter following the initial rapid loss."

All the experiments described so far have been in the low-temperature carbonisation range of 300-700°C. The range 700-1100°C has been studied by Peters[114], who injected coal into a large, vigorously stirred mass of granular corundum, preheated to the required temperature. Volatile evolution was measured by collection of the volatile products at 0.5 second intervals. (This system of carbonisation has been developed commercially as the L-R (Lurgi-Ruhrgas) Process[115].)

The data showed a very rapid initial gasification rate, lasting about 1-3 seconds, and the majority of the volatile evolution within 3-6 seconds, for temperatures of 1100-700°C respectively in both cases. Moreover, the rate of evolution was constant over the first, and major, portion of the curve, during which about 75% of the volatile evolution occurred, i.e. the reaction is of zero order. The activation energy for this stage was found to be only 2.6 Kcal/mole, which implies that the rate-governing step was of a physical rather than a chemical nature, at high temperatures. Peters postulated that at these temperatures the rate of volatile emission is governed by the rate of distillation of the metaplast from the coal particles, and that owing to the latent heat demand the coal particle surface remained at 350°C until all the metaplast had been evaporated and possibly cracked. This does not conflict with the theory of van Kevelen et al (derived from slow primary degasification below 500°C) that the primary decomposition of coal first produces metaplast, but indicates that at temperatures above 700°C the physical process of evaporation may be the slowest, and hence the rate-controlling factor. According to Yellow[160], however, the results of Peters are open to doubt, in that the rate of heat transfer to the particles of coal may have been the controlling factor, rather than the rate of evaporation of metaplast; the coal would

therefore be at an unknown temperature during this early stage of devolatilisation.

It appears, then, that carbonisation under conditions such that heating is extremely rapid, gives rise to very considerable changes in the composition of all of the products, compared with the products of slow "conventional" coking. To evaluate the effect of such changes on the sulphur content of the residual coke, it is now necessary to summarise published information on the behaviour of coal sulphur during rapid carbonisation.

VIII. Behaviour of Coal Sulphur during Rapid Carbonisation

The first experiments of this type were carried out by Snow[136] in 1932, who dropped 20-40 mesh coal down a 1.5 in. dia. by 4 ft long tube furnace, against a countercurrent stream of hydrogen. Only two runs were reported; for a furnace temperature of 1000°C and a coal feed of 130 gm/hr the results were as follows.

Table 4

Hydrogen flow, cfm	% Loss in wt	% sulphur in residue	% sulphur removal
0.0137	41.1	3.99	56
0.0183	39.9	3.64	59

The additional desulphurisation due to the increase in hydrogen flow rate may be due to the consequent increase in residence time; it is not unlikely that any difference is masked by the experimental errors inherent in this type of work. No details are given as to the relative proportions of organic and mineral sulphur in the coal or coke.

As part of an investigation into the differences in the carbonisation behaviour of coals for rapid and conventional (slow) coking processes, Chukhanov[32] et al describe the change in elemental composition of a coal, in terms of its carbon, hydrogen, sulphur and(oxygen + nitrogen) contents. (Fig. 5) Unfortunately, the results

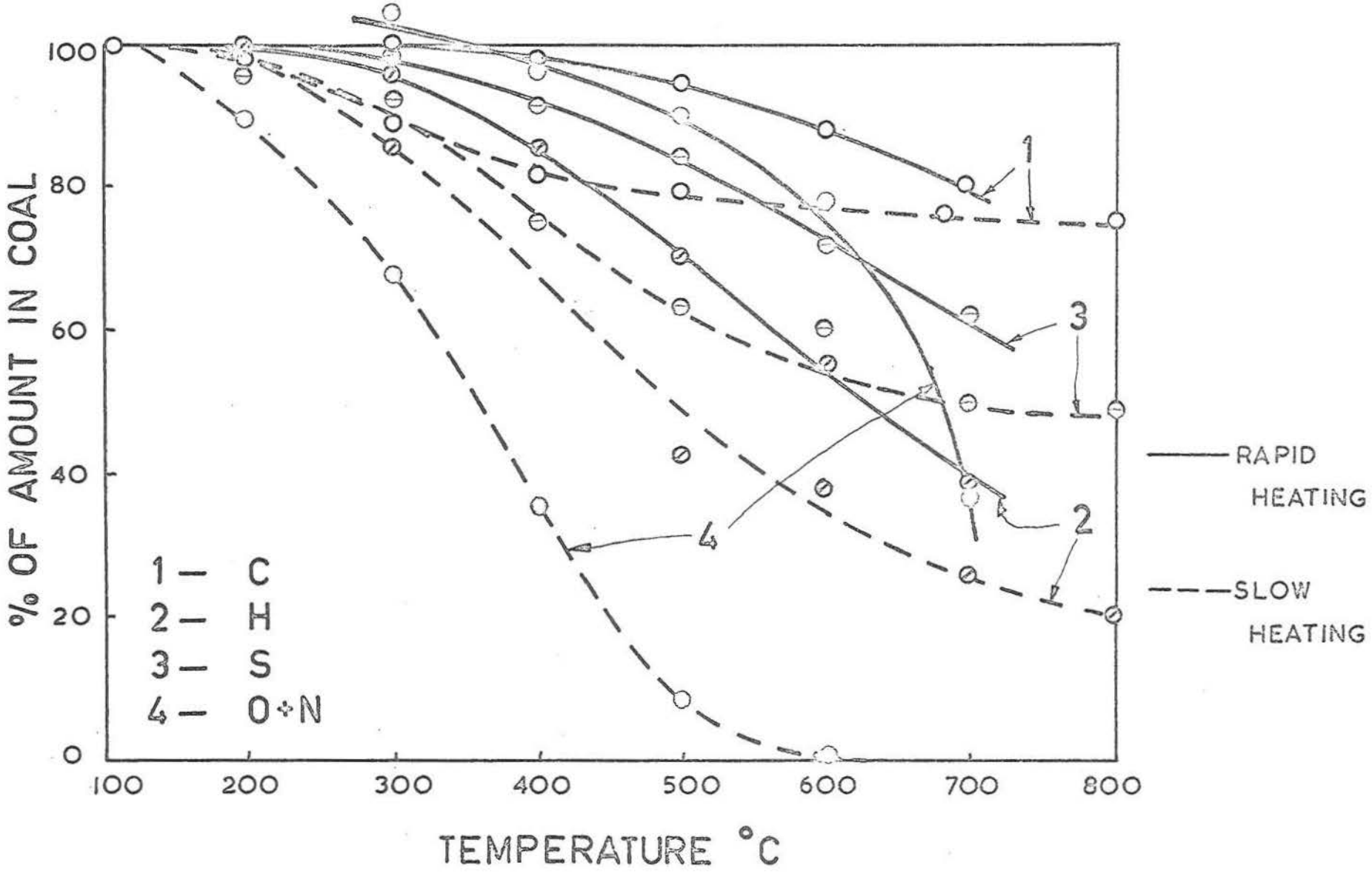


FIGURE 5 ELEMENTAL COMPOSITION OF CHARS FROM RAPID AND SLOW CARBONISATION OF SUB-MOSCOW COAL (CHUKHANOV[32])

are not reported in full, the data obtained referring only to a time of 0.35 second, for the rapid carbonisation process. Thus, the two processes cannot be properly compared, since in a previous paper of Chukhanov[30] it was reported that most of the sulphur compounds are given off in the second main stage of rapid carbonisation, between 0.1 second and 2-3 minutes. However, the extent of sulphur removal during this very short carbonisation indicates that appreciably greater desulphurisation might be possible with longer contact times.

The most valuable work, although in an associated field, has been carried out by Kaliuzhnyi[82], a co-worker of Chukhanov, on the behaviour of the different forms of sulphur during the rapid pyrolysis of a Volga shale, containing 4.2% total sulphur, of which 11.9% was sulphate, 32.4% pyritic and 55.7% organic sulphur. The temperature range studied was 310-520°C, with times of heating of 0.15 second, 5 and 20 minutes, and 4 hours. The results for the influence of temperature on the total sulphur in the residual shale are shown in Fig. 6.

The shaded portion at the top of the graph represents the original sulphate sulphur, claimed to have been leached out by the quench water. However, it should be noted that under coking conditions, sulphates are at least partially reduced to the corresponding sulphides[91,113], so the quantity of sulphate in the shale would certainly

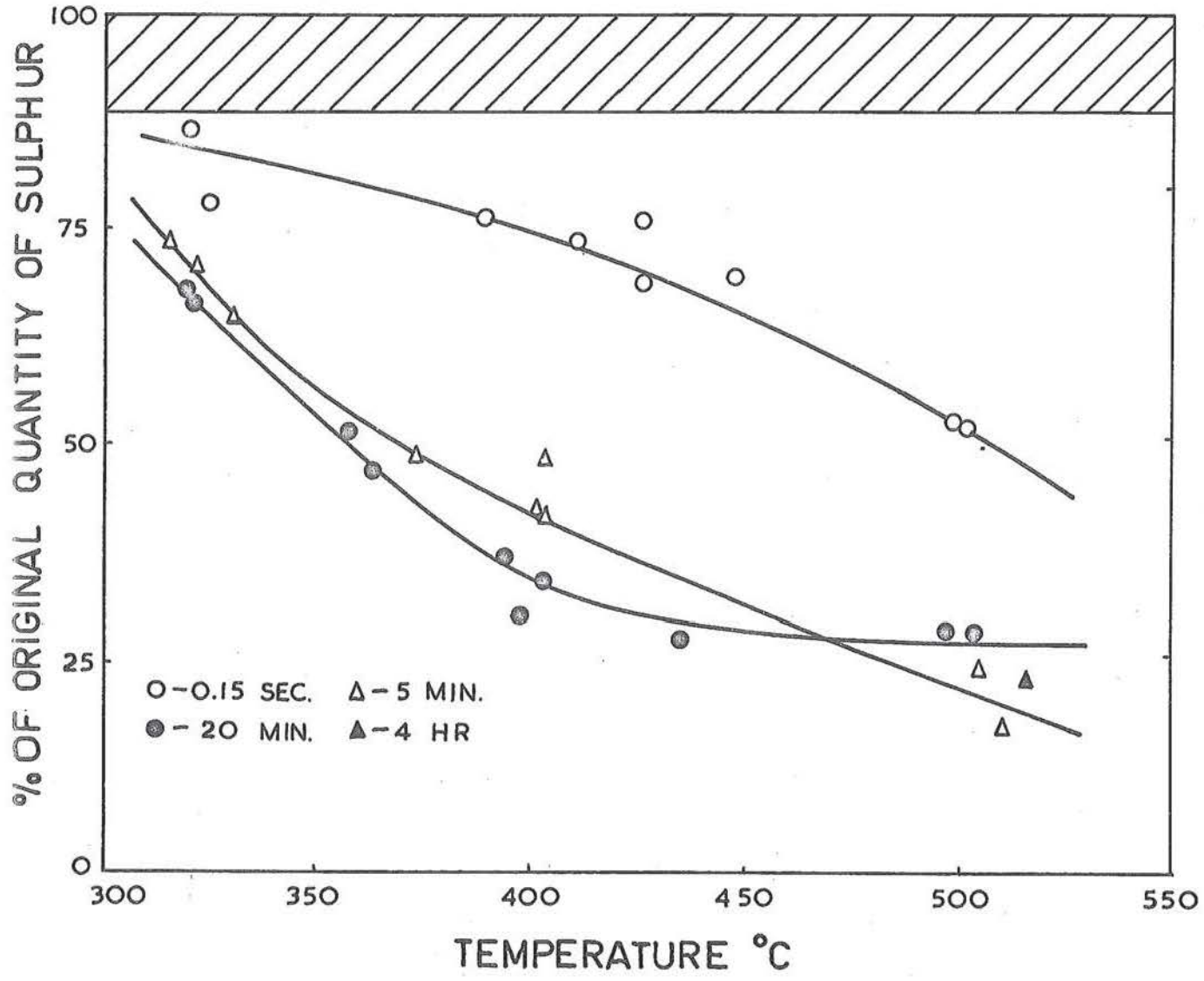


FIGURE 6 EFFECT OF TEMPERATURE AND CARBONISATION TIME, ON TOTAL SULPHUR CONTENT OF SHALE RESIDUE (KALIUZHNYI[82])

not remain constant under the conditions described.

The graph supports the conclusion of Chukhanov[30], that the liberation of sulphur during the first stage (0-0.1 second) of rapid carbonisation of coal is small, the main products being formed during the second (up to 3 minutes) stage. The fact that the curves for 5 and 20 minutes cross at high temperature indicates that the scatter of results due to experimental error may be such that there is little significant difference between the result for 5 minutes decomposition, and that for longer periods, at temperatures other than about 400°C. Alternatively, the emission of volatile matter above 450°C may have continued after sulphur volatilisation had ceased. No experiments were reported at temperatures above 520°C, but it seems probable that further desulphurisation would have resulted.

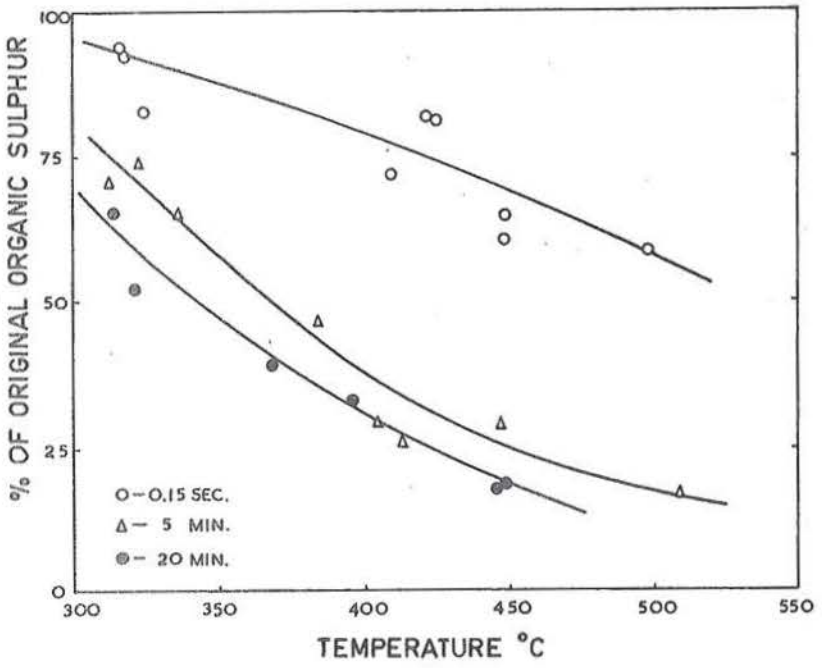
Unfortunately, no comparative results are available for the slow (conventional) retorting of this shale, but the author compares his results with those for a similar shale, indicating that with rapid heating the extent of desulphurisation is appreciably greater at temperatures less than 450°C, but above this temperature the advantage may be relatively small.

Kaliuzhnyi also carried out a series of experiments to determine the effects of temperature and coking time on the distribution of individual varieties of sulphur

between solid and volatile products. As in the earlier series of experiments, the sulphate sulphur content was assumed to be constant, and hence the results are not complete. However, some interesting conclusions may be drawn from the behaviour of the other components. (Fig. 7)

It is apparent that the initial generation of organic sulphur proceeds very rapidly indeed - at 450°C after 0.15 second, about one-third of the original organic sulphur is volatilised. It is also apparent that the later stages of volatilisation of organic sulphur proceed very much more slowly. In fact, the initial rate of decomposition apparently exceeds that in the following period by more than a thousand times. The author suggests that this can only be explained if the decomposition of organic sulphur can be considered as occurring in two separate stages, or that two different compounds or groups of compounds decompose, with widely differing kinetic characteristics. (In this context, it should be remembered (see earlier) that organic sulphur in coke may be derived from either organic or mineral sulphur in the original coal.)

As can be seen from Fig. 7, the decomposition of pyritic sulphur proceeds slowly at temperatures below 330°C, but with increase of temperature above 400°C more than half of the original material is decomposed within 5 minutes. Above 450°C, it appears that the equilibrium



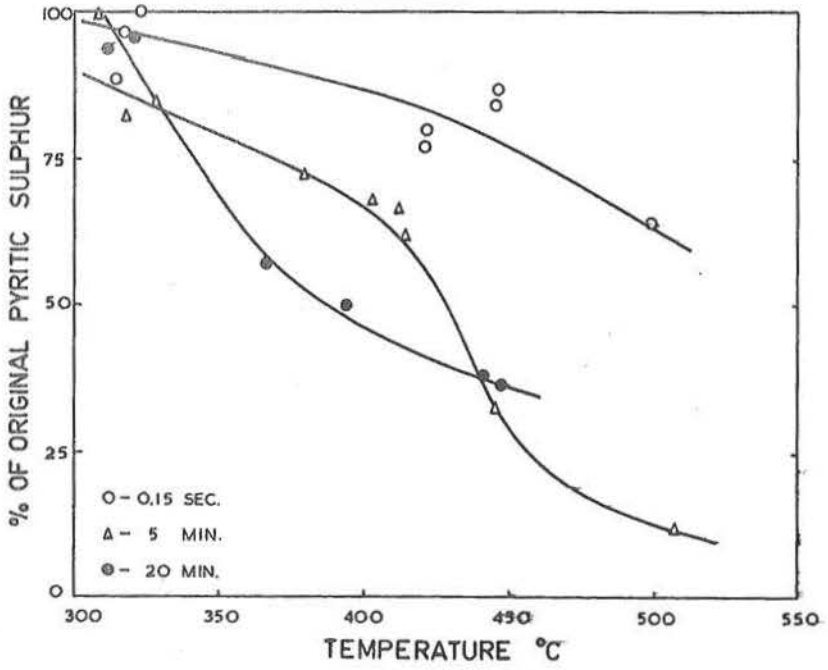


FIGURE 7 ORGANIC AND PYRITIC SULPHUR CONTENTS OF SHALE RESIDUE (KALIUZHNYI[82])

is reached in rather less than 5 minutes, the change in shape of the curve indicating a possible change in the process of decomposition of the pyrites. It seems highly probable that, at temperatures higher than about 550°C, virtually all the pyritic sulphur would be decomposed within 5 minutes coking time.

Slight generation of ferrous sulphide, up to 5% of the total sulphur, is reported at temperatures above 400°C, but this is very much less than would be expected if pyrites decomposed directly to FeS or to pyrrhotite[29, 121]. Therefore, it appears possible that pyrites decomposes directly to free iron, the sulphur being volatilised, or else combining directly with the hot coke. Since decomposition of pyrites continued to proceed rapidly above 500°C (at which temperature the evolution of other volatile matter is appreciably reduced), and the curve of organic sulphur content shows no irregularity, it is not unlikely that the sulphur has been volatilised, possibly as carbon disulphide[70]. However, as has been noted earlier, the method of analysis for pyrrhotite in coal may be unreliable in the presence of quantities of organic sulphur, so the possibility of analytical error cannot be discounted.

The work of Kaliuzhnyi provides the only detailed information available in the literature regarding the behaviour of sulphur during rapid coking. Although

confined to shale, rather than coal, it is not unreasonable to use the results as a guide to the behaviour of the forms of sulphur in the rapid coking of high-sulphur coals.

IX. Previous Work and Construction of Apparatus

Work in the Department of Chemical Engineering, University of Canterbury, on the behaviour of sulphur during carbonisation was started by Collins[36] in 1959 under the direction of Professor S. R. Siemon. Siemon and Collins designed and built a small fluidised sand bed, heated by gas from another bed mounted immediately below, in which was immersed an electrical heating element (Fig.8). Coal injection was via the glass bypass line, pressure drop across the porous distributor plate being sufficient to ensure adequate gas flow through the injector.

Although this stage was not reached by Collins, it was planned that coal would be carbonised in atmospheres of various reducing gases, the outlet gas being analysed for sulphur compounds. The residual sulphur in the coke would be obtained by passing air through the bed, the outlet gas again being analysed, this time for sulphur oxides and carbon dioxide, the latter to obtain a value for the quantity of coke produced, and the sulphur/carbon ratio in the coke.

The work was continued by Watson[151] in 1961, who refined the original equipment and extended it to include purification of the supply of coal gas, which was the reducing gas to be used in the first series of experiments. Watson also constructed an analysis train, and took the project virtually to the stage at which experimentation

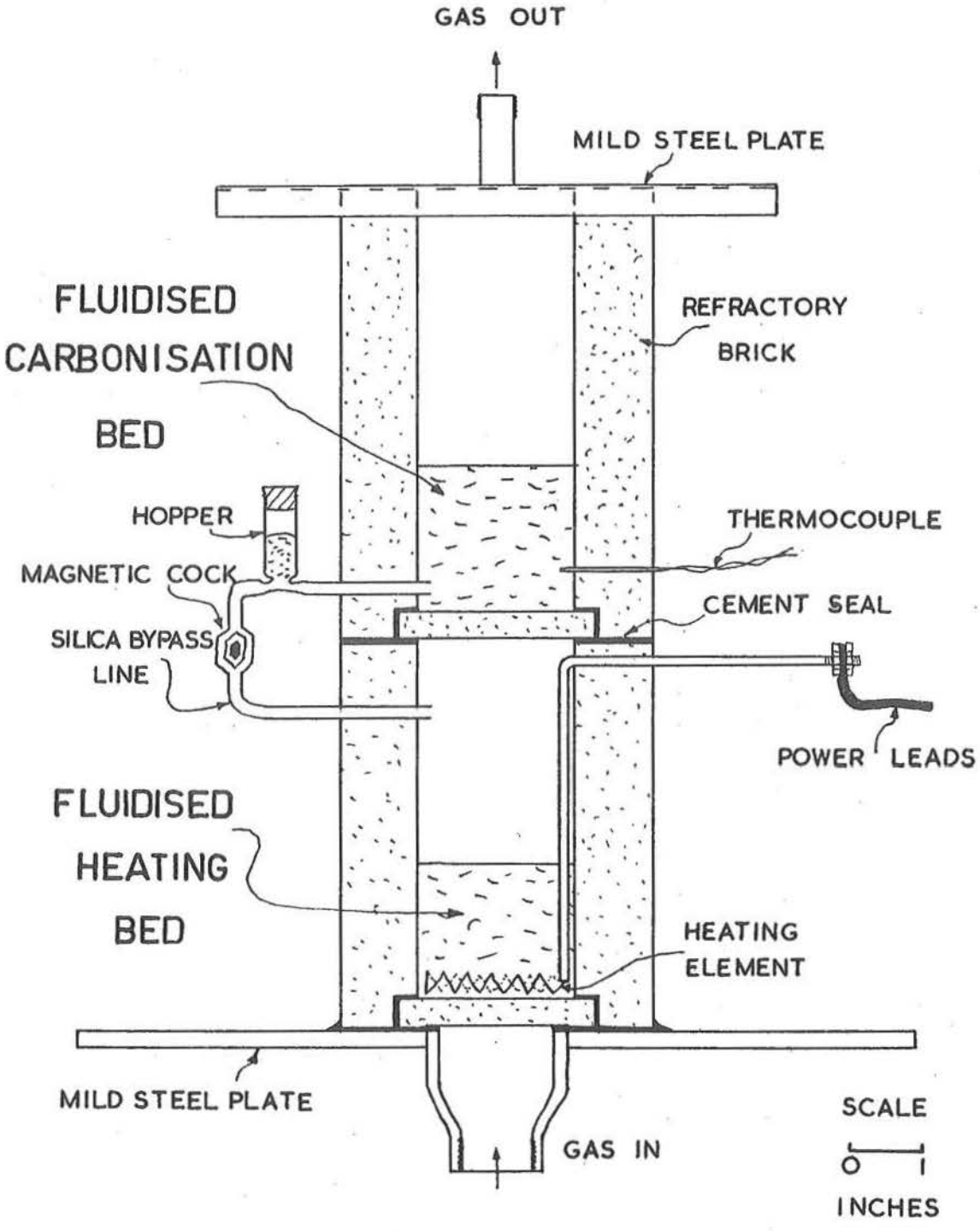


FIGURE 8 FLUIDISED SAND BED CARBONISATION APPARATUS (COLLINS[36])

could commence.

A flow diagram of the apparatus is shown in Fig. 9. Since coal gas contains some sulphur compounds, Watson installed an activated carbon adsorber to remove thiophene, and a tube furnace packed with a sulphur-acceptor[100], to remove any other sulphur compounds. The coal injector and furnace were also modified (Fig.10), the injector constructed by Collins being found to be unsatisfactory in operation.

The outlet gas from the bed was to be analysed by absorbing the hydrogen sulphide in zinc acetate solution, the quantity being determined by the methylene blue method[99].

In order to ensure that all volatilised sulphur was in the form of hydrogen sulphide, the gas was first passed through a tube furnace packed with chips of fused silica. The intention was that, in the presence of a large excess of hydrogen from the coal gas, all high molecular weight compounds (e.g. tars, etc) would be cracked and reduced to simple saturated hydrocarbons, and all complex sulphur compounds to hydrogen sulphide[151].

It was at this stage in the project, at the beginning of 1962, that the writer commenced work, under the direction of Professor Siemon.

Watson's plans were followed in making the first trial runs. Unfortunately, trouble was experienced

due to a number of factors, the first of which was sticking of the coal in the injector tube. This tube entered the bed through the top plate and hence was heated by the gas flow for most of its length. Although the gas used to drive the coal was cold, it appeared that, due to contacting the sides of the tube, the coal was heated to its melting point before expulsion into the bed, with consequent rapid blocking of the tube. Use of higher gas flows partially resolved the problem, but at the cost of serious disruption of the flow pattern in the fluid bed. However, it was noted that the evolution of volatile matter from the bed occurred very rapidly, after injection - within two or three seconds, at a temperature of about 700°C.

Another problem was that it proved virtually impossible to seal the firebrick walls of the fluid bed, and thereby prevent leakage of gas. Cement washes had little effect, so an attempt was made to seal the porous brick with sodium silicate solution, which penetrates the pores and dries to a hard, heat-resistant, impermeable skin. Some success was achieved, but the problem then arose of preventing the sodium silicate from sealing the porous bases of the fluid beds, whilst retaining a good seal on the outside of the apparatus. Despite a number of attempts, the solution to this problem did not present itself.

A further difficulty with the original equipment was that of ensuring adequate heating of the bed. The heating element was redesigned following the advice of Mr G. Dawson (Gus Dawson and Co., Christchurch), but it appeared that, in order to obtain high temperatures in the upper bed, the element in the lower bed had to be run under conditions that rapidly resulted in the burning out of the wire. The difficulties will be appreciated when it is realised that up to 1 Kw of heat was being dissipated in a fluid bed 2" dia. by 2" high, at temperatures in excess of 1000°C.

For these reasons, it was decided to completely redesign the apparatus using Incoloy DS as the constructional material, as originally suggested by Collins. This metal (a nickel-iron-chromium alloy, manufactured by Henry Wiggin and Co.) is capable of operation under oxidising and reducing conditions at temperatures up to 950°C, and is resistant to attack by sulphur.

The new apparatus was constructed as shown (Fig.11) and heated by a 6" long by 2½" I.D. tube furnace. The fluid bed was made in two sections so that the distribution grid could be removed if required and so that the assembly could be installed in and removed from the tube furnace when necessary.

The coal injection tube entered from underneath the bed, and was immersed in a small trough of water

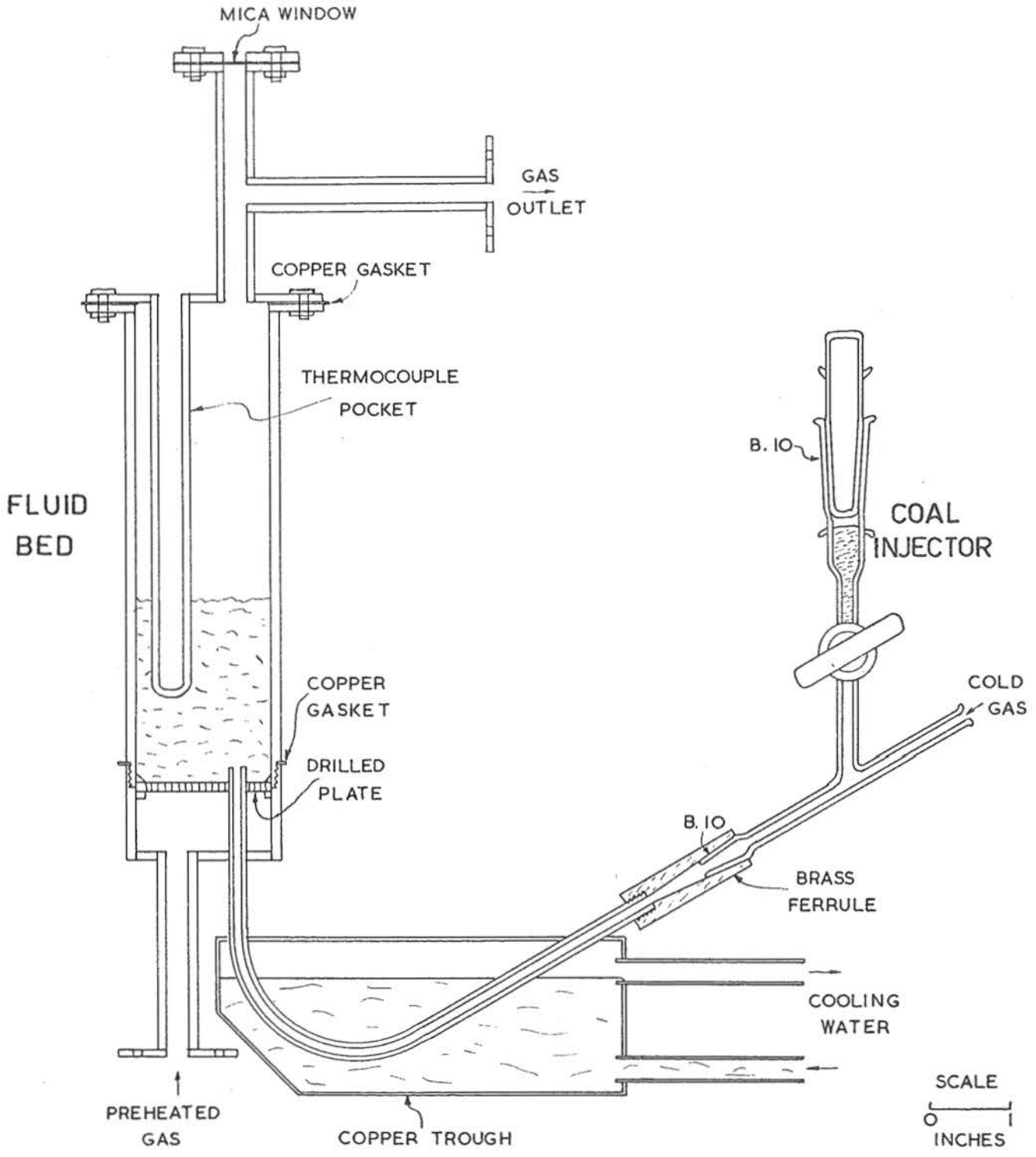


FIGURE 11 INCOLOY DS FLUID BED APPARATUS, WITH PYREX COAL INJECTOR

so that the coal and gas could be kept cool until the last moment before injection. By this means, it was hoped to prevent blockage of the inlet tube.

The main flow of fluidising gas was preheated in an Incoloy DS tube filled with ceramic beads, mounted in a tube furnace. The exhaust gases from the fluid bed passed through a further tube of Incoloy, packed with chips of fused silica, as specified by Watson.

It was decided that during the initial stages of the work hydrogen rather than coal gas would be used, both for the sake of simplifying the apparatus and to eliminate the need for removal of sulphur compounds from the inlet gas. Hydrogen also has the advantage of being pure; the use of coal gas would introduce additional sources of variation to the experimental work.

A diagrammatic view of the apparatus (Fig. 12) shows the disposition of the main items, together with ancillary equipment such as recorders, flowmeters, etc. (Also see Plates 1 and 2.)

On the basis of the experience gained with the earlier equipment, it was realised that the analysis train, designed by Watson, would not be satisfactory for two main reasons.

Watson assumed that the sulphur would be generated at a fairly uniform rate over a period of 10 minutes, and on this basis found that, for 1 gm of coal injected,

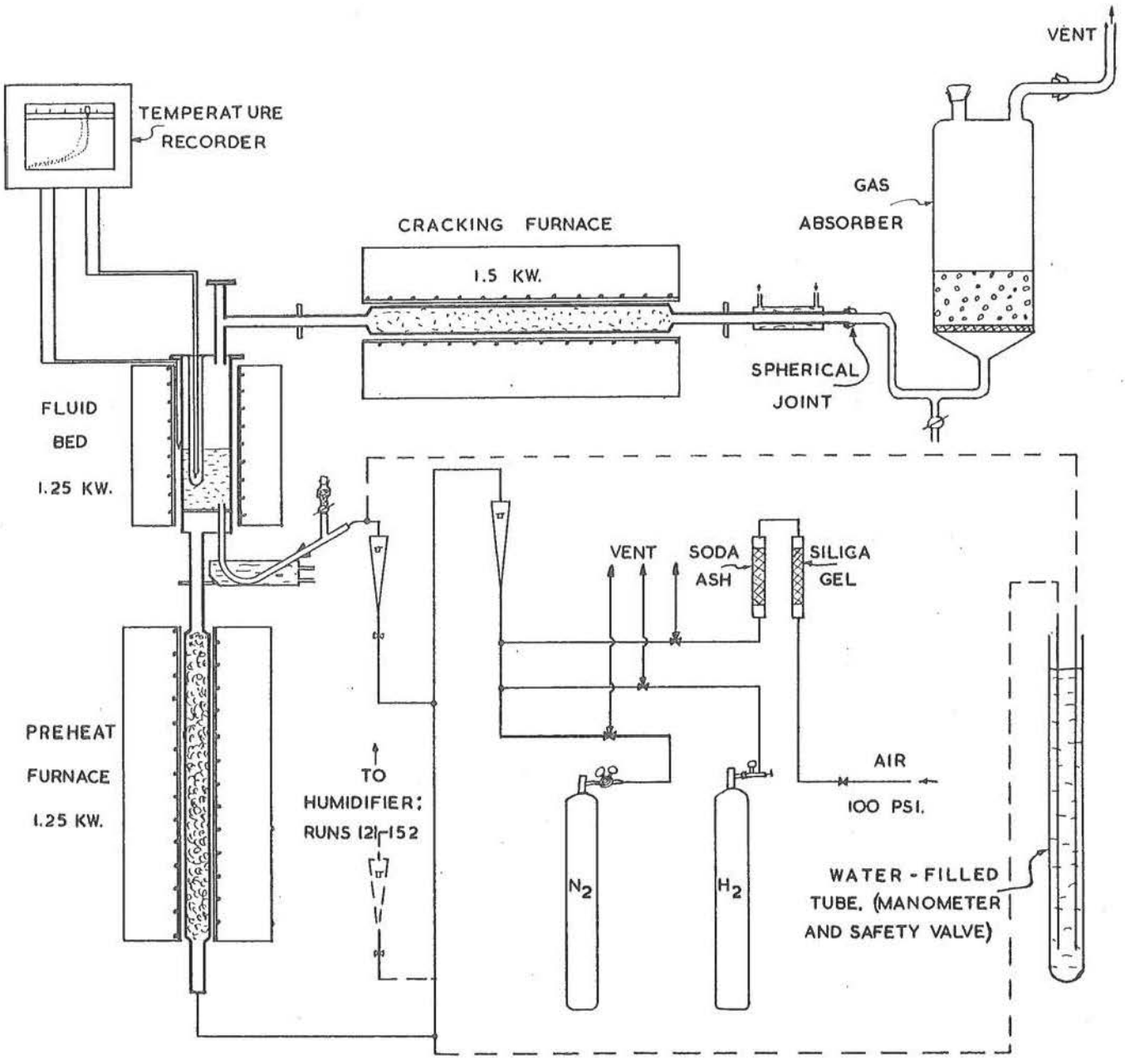
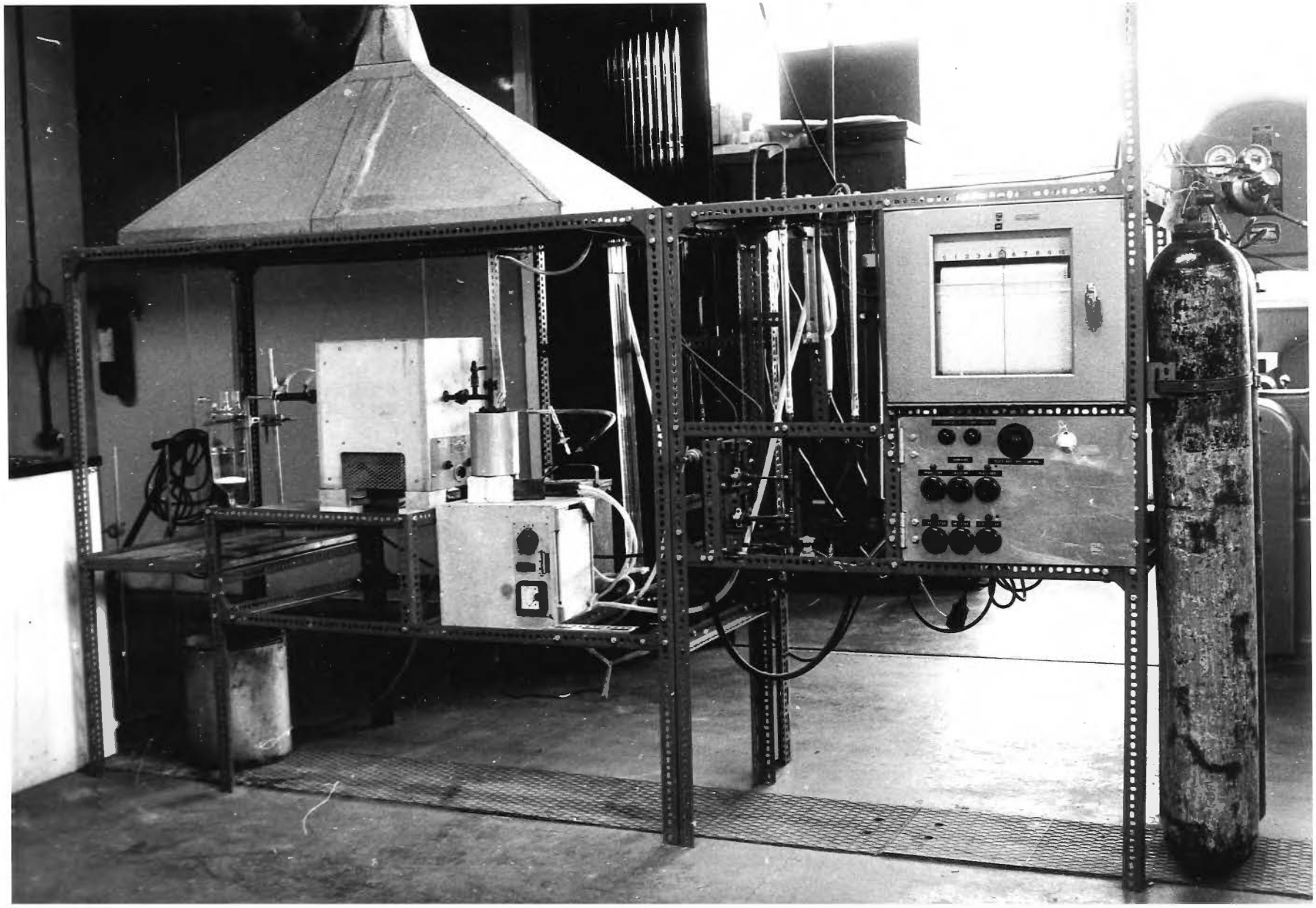


FIGURE 12 FLOW DIAGRAM OF APPARATUS.

Gallenkamp



the expected concentration of hydrogen sulphide in the outlet gas from the bed would be about 0.0001 gm/l. This very low concentration could only be detected by the most sensitive techniques, such as the methylene blue method. However, initial experiments showed that the main evolution of volatile matter occurred over two or three seconds, which meant that the concentration of hydrogen sulphide in the outlet gas would be, momentarily, very high indeed, and certainly of the order of 0.01 gm/l.

Another factor was that this rapid evolution of volatiles caused a violent short fluctuation in total outlet gas flow, and any method of sampling of part of the outlet gases must be capable of sampling an accurate proportion of the gas during this short fluctuation. It was therefore considered that Watson's original design (perfectly adequate under the conditions for which it was designed) would have to be modified to be capable of analysing the entire outlet gas stream for hydrogen sulphide.

To this end, an absorption vessel was constructed of Pyrex glass (Fig. 12), using a coarse grade sintered glass filter funnel as the base, through which the gas stream would pass into the absorption solution. The absorber was of large (3") diameter to reduce the superficial gas velocity and thus prevent excessive frothing and entrainment of the absorption solution.

To control the temperature of the absorption solution, the base of the absorber was immersed in a bath of cooling water during each run. Spherical ground glass joints were used on the gas inlet and outlet, enabling gas-tight connections to be maintained, and at the same time giving mechanical simplicity and flexibility.

The high concentrations of hydrogen sulphide in the gas meant that a less sensitive and laborious analytical technique than the methylene blue method would be preferable. The method chosen was the use of cadmium chloride as the absorption solution, from which hydrogen sulphide precipitates cadmium sulphide. This is easily determined by addition of excess iodine solution, acidification with concentrated hydrochloric acid, and back-titration with sodium thiosulphate solution. This method had the advantage of being capable of extension, as required, to incorporate analysis of a variety of other sulphur compounds found in gas. (The procedure will not be described further, since it is not unconventional and is given in great detail by Mason and Hakewill[101].)

The coal injector (Fig. 11), made from Pyrex glass, was similar to that designed by Watson, with modifications to permit easy removal and weighing before and after each run, to determine the actual quantity of coal injected. It was decided to maintain a steady flow of

gas through the injector during each run; this would help to reduce momentary disruption of the fluid bed flow pattern during coal injection.

X. Experiments - Series I

The apparatus being basically complete, some trials were carried out with the top of the apparatus removed (permitting observation of the behaviour of the bed), to determine the optimum gas flowrates, over the temperature range of interest. Since the thermal expansion of the gases was considerable at the operating temperatures of the bed, these optimum flowrates varied correspondingly. For the first trials, the graded sand prepared by Collins and Watson was used.

Once the required flowrates were known, the equipment was completely assembled and some trials made with injection of the coal and analysis of the product gas for hydrogen sulphide. The coal used in these trials was Stockton B-tunnel, of 1.2% total sulphur (virtually all organic), swelling number 9, volatile matter 33%, and negligible ash content. The temperatures used were about 700°C.

This series of experiments will not be described individually, since many proved abortive, and only general conclusions could be drawn from the results. (See Appendix for complete table of results.)

During the first few runs, difficulty was experienced in that blockages occurred due to coal sticking in the inlet pipe. The only remedy for a blockage was to change the gas flow back to air (using nitrogen to flush

made with different levels of carborundum in the fluid bed (to reduce pressure drop in the injection line) and even with the bed material completely removed from the apparatus. In the former case, little difference was observed, and in the latter the coal immediately stuck to the hot metal walls with no reaction in the absorber.

It was also noticed that, even when a small quantity of coal did enter the bed, agglomeration took place due to adhesion of particles of carborundum to the molten coal, with consequent loss of fluidisation.

Since these problems obviously resulted from the swelling properties of the Stockton coal, a sample was obtained of coal from the Dauntless mine, of swelling number less than 1, and total sulphur content 5%, mainly organic.

Injection of this coal (-60+85 mesh) was fairly uneventful; only slight blockage occurred, and a substantial reaction was noted in the absorber. There was also considerable deposition of tar and soot in the absorber, with partial blocking of the sintered glass plate. In subsequent trials smaller quantities of coal were injected, usually of the order of 0.1 gm.

In order to increase gas velocities still further, the 60 mesh carborundum in the fluid bed was replaced by silicon carbide of about 40 mesh grade. This change proved successful, no blockages being observed during

injection of a further sample of the Dauntless coal.

The success observed prompted retrial of Stockton coal, and it was found that -44 +52 mesh grade could be injected without blocking the inlet line, provided this was done very slowly so that only a thin stream of coal was entering the bed. Some agglomeration of the bed was noticed, but with the relatively violent agitation caused by the high gas velocities, this soon broke up if the coal injection was stopped for a while.

The quantity of sulphur present in the absorber solution was determined first in Run 32, and was found to be greater than the maximum possible evolution of sulphur from the sample of coal injected into the bed. Analytical errors were discounted, and the remaining likely explanation was that carbon deposition (from tars, soot, etc, in previous runs) had occurred in the outlet lines from the fluid bed, and sulphur had been absorbed by this carbon. When hydrogen was passed through the apparatus, immediately prior to the run, the hydrogen reduced the absorbed sulphur to hydrogen sulphide, which then reacted with the absorption solution. That this was, in fact, the correct mechanism was proved some time later by passing hydrogen through the equipment for about three hours, after which time the evolution of hydrogen sulphide was still detectable, although very small. In all runs subsequent to Run 90, hydrogen was

passed for at least 5 minutes before and after each run to make reasonably sure that most of the sulphur had been eliminated. Although only three attempts (Run 57-59, all unsuccessful) were made to obtain the sulphur content of the char by analysis for sulphur dioxide, the char was always burnt off after a run by reverting to a flow of air.

About this time, it was noticed that the pressure drop over the apparatus had substantially increased, and the equipment was dismantled to determine the cause. The tube packed with silica chips was found to be blocked with fine carborundum particles, carried over from the bed by the gas stream. The packing was removed, sieved to remove the fine particles, and replaced. This problem persisted,to a greater or lesser extent depending on the gas flowrates used, until the end of the series of experiments; no remedy was found, other than periodically dismantling and cleaning the tube. An attempt was made to clean the gas of these entrained particles by installing a small cyclone collector inside the apparatus (Fig. 13), but with no success. The cyclone rapidly blocked, and the entrainment was then worse than before.

A number of further attempts (Runs 35-59) were made to carbonise Stockton coal, but in all cases agglomeration occurred in the bed, although in most cases it was

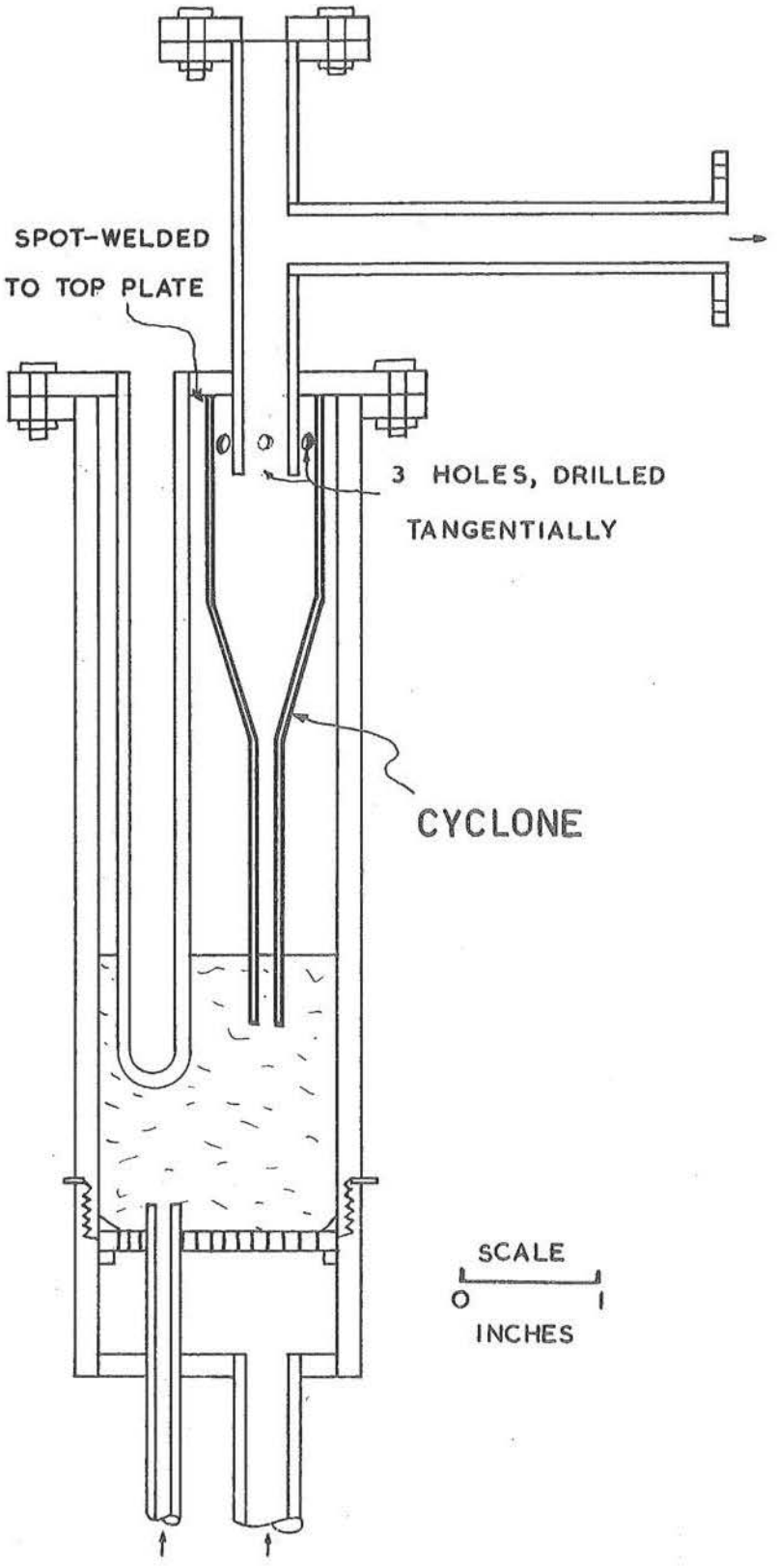


FIGURE 13 DETAIL OF CYCLONE COLLECTOR (FITTED TEMPORARILY)

possible to analyse the product gas for hydrogen sulphide. Results varied from 0.1 to 1.2% of the weight of the coal, which itself contained 1.2% sulphur. There was no real pattern observed in the variation of the values of sulphur obtained, other than that, apparently, a rapid blockage generally gave rise to a small amount of sulphur detected, and vice versa. It does not seem improbable that the agglomerated bed provided a barrier of mainly carbonaceous matter to the outflow of volatile matter from the coal, resulting in absorption of the sulphur compounds by the hot coke.

At this stage (Run 52) it became necessary again to dismantle the silica-packed tube for cleaning. While dismantled, it was observed that many of the silica chips were black in colour, indicating that carbon deposition had not burnt off. Prolonged oxidation was required to burn off the carbon, and in any case it is likely that, during carbonisation of the next coal sample, further deposition would occur, with consequent sulphur uptake. For this reason, a number of runs were done (54-83) with the silica tube removed, and the absorber connected directly to the outlet gas line, via the short, water-jacketed extension tube.

To reduce the problems associated with the use of high-swelling Stockton coal, it was decided to revert to the use of Dauntless, as from Run 60.

Some trouble was experienced in the analysis of the solution from the next few runs, later attributed to deficiencies in the purity of the laboratory deionised water supply. Fresh supplies from an alternative source solved this problem, but highlighted yet a further difficulty in the analytical method (Runs 56-65), namely an inconsistency in the titration of iodine with the absorber solution.

Upon adding iodine to the absorber solution, no colour change was apparent until several mls had been added. It was possible to carry out an initial titration of the iodine with the absorber solution before the usual procedure of adding excess, plus concentrated hydrochloric acid, and back-titrating. This initial titration could not be taken to a stable end-point, which indicates that the iodine in solution was reacting with the sulphide ions, the solubility product causing the equilibrium to be displaced in such a way that more cadmium sulphide went into solution, and so on until all the precipitate had dissolved and reacted with the iodine.

However, this mechanism does not account for the relatively large initial iodine reaction. It is probable that this was due to other products of carbonisation dissolved in the absorber, capable of being oxidised by the iodine. Because these two effects were not separable, no allowance could be made, and it was

decided to delay investigating further until a reproducible performance was obtained from the fluid bed.

From the quantities of tar, soot and smoke found in the absorber after injection of the coal - especially when a given amount had been injected rapidly - it was obvious that, whether with or without the silica tube furnace, the carbonisation products were not being properly cracked and reduced, and were either settling out in the outlet lines from the bed or in the cracking furnace, or else going unchanged into the absorber where, in the case of complex sulphur compounds, no reaction was possible with cadmium chloride, thus giving a false result. A number of variations (Runs 75-83) in the method of operation of the equipment were then tried to determine whether it was possible to gain some idea of the conditions under which the retention of sulphur could be minimised.

The removal of the cracking furnace did not prove entirely successful - due to increased fouling of the absorber solution - so it was replaced. Shortly afterwards, it was decided to try the introduction of a small bleed of steam into the line between the fluid bed and the cracking furnace. It has been suggested[101] that this prevents deposition of carbon, and hence the uptake of sulphur.

The equipment was modified (Run 96) as shown in Fig. 14, the water droplets being vaporised by contact with the hot metal tubing. An appreciable increase in the detected sulphur was obtained, but the precision of the results was no better, apparently identical runs often giving widely different results.

Since it was thought that the water injection might be giving rise to excessive local cooling of the apparatus, a further modification was installed (Fig. 15) (Run 121), whereby a stream of the gas was humidified in a bypass line by being bubbled through a flask of hot water. No improvement was noted, so the temperature of the bypass stream was raised by coiling an electrical heating element (threaded through ceramic insulating beads) around both the final section of the bypass line (constructed of Inconel) and the connecting line between fluid bed and cracking furnace.

Reproducibility of the subsequent runs was slightly improved, but was still quite unsatisfactory. Various bypass gas flowrates were tried, gas compositions varying from pure gas to pure steam (by boiling the water in the flask), and with degrees of superheat up to the maximum running temperature of the tube heater (about 900^{o}C), still with little effect.

The silica chips were then replaced with small (1/8") ceramic insulating beads to determine whether catalytic effects were possible, but with no significant

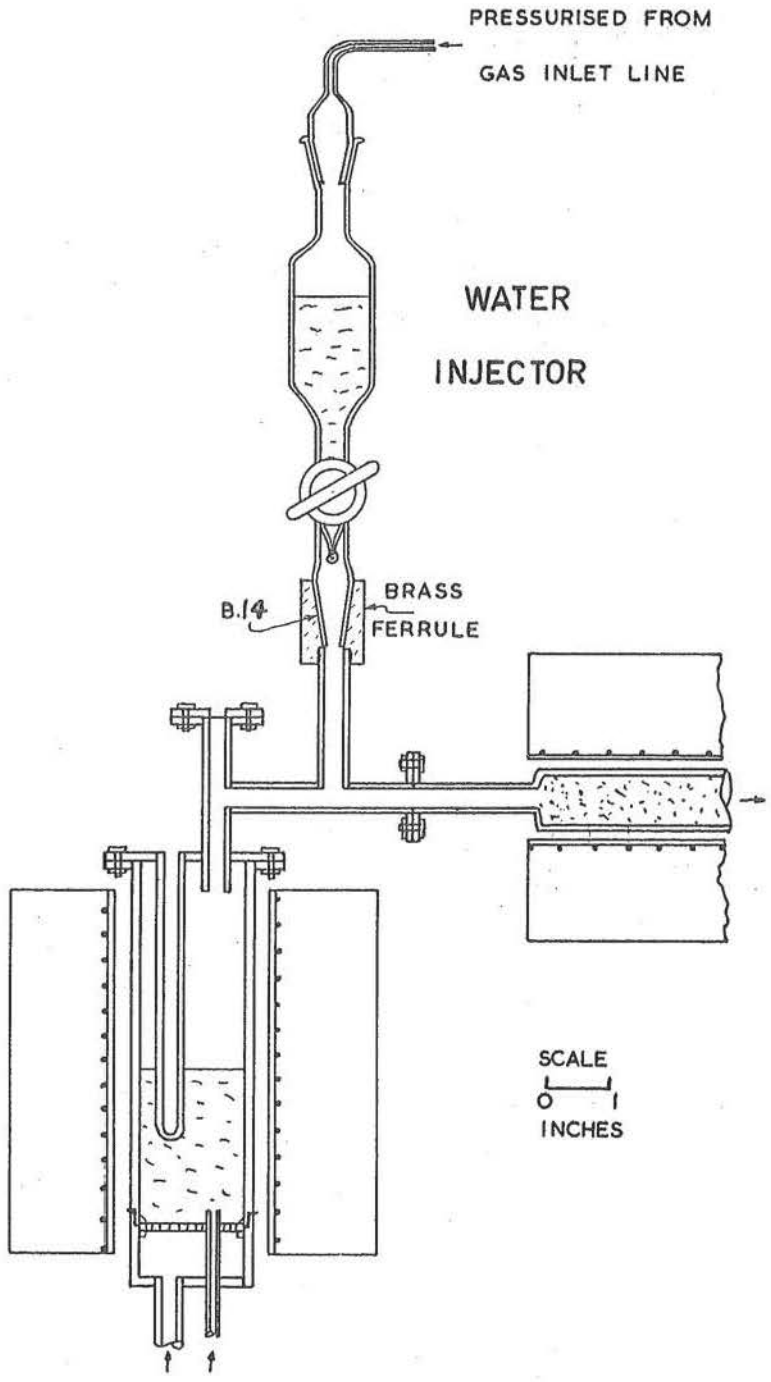


FIGURE 14 DETAIL OF WATER INJECTION MODIFICATION

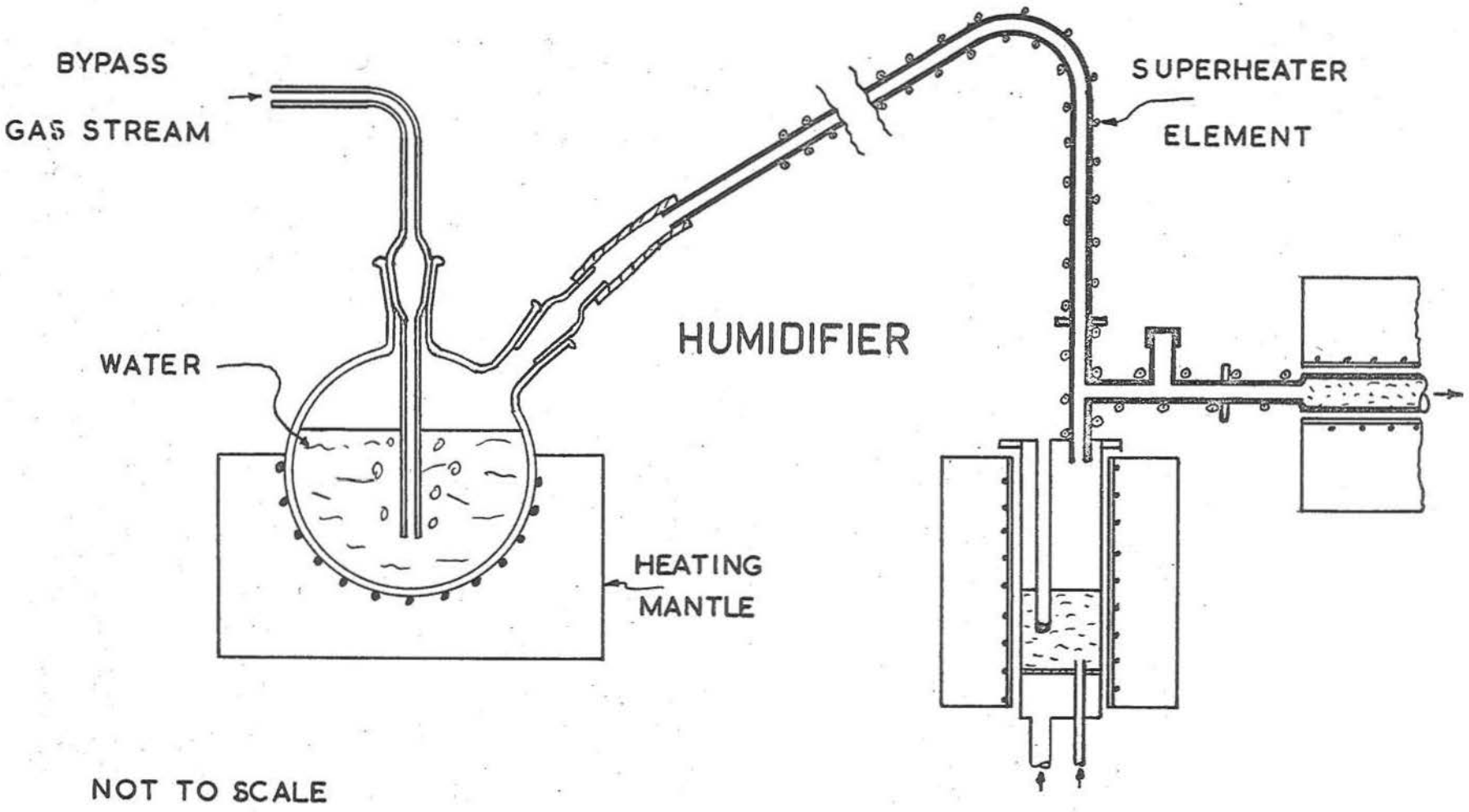


FIGURE 15 DETAIL OF BYPASS GAS HUMIDIFIER AND SUPERHEATER ARRANGEMENT.

change. Fresh silica chips were then tried, again with no noticeable result.

In order to overcome the problem of tar deposition, an investigation was made of the possibility of using another method of analysis for the raw gas from the fluid bed. The only reasonably feasible technique was combustion of the entire gas stream in oxygen, with subsequent absorption and determination of the sulphur oxides. The method had to be rejected, since the burner required to handle the gas flowrates used (of the order of 1 cu.ft/min of hydrogen) and the heat release (up to 20,000 BTU/hr) would be too large and cumbersome. In addition, the dangers of burning hydrogen and oxygen in other than small equipment are well known.

At the time when experiments were being made with the silica tube furnace disconnected, it was observed that, under conditions of high gas flow it was possible to elutriate a mixture of carborundum and char from the bed. As an alternative approach to the problem, it was decided to attempt the collection of coke elutriated from the bed, with screening if necessary, to remove carborundum from the product. A small glass cyclone was therefore constructed (shown in its final form, Fig. 16) to collect the product.

A few trials (Runs 153-160) were made, and it was

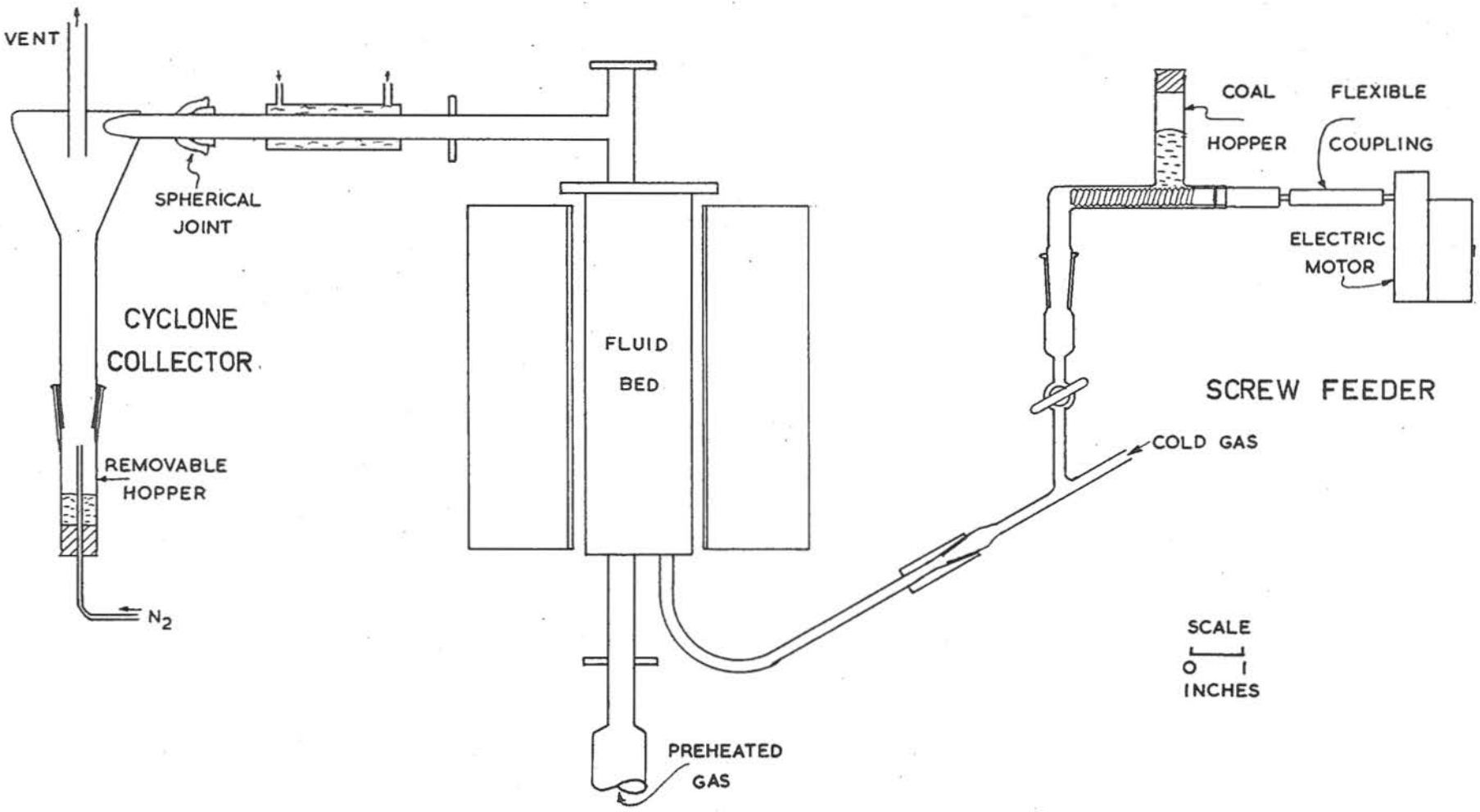


FIGURE 16 CONTINUOUS FLUID BED CARBONISATION APPARATUS (SERIES II)

found possible to obtain char without elutriation of any bed material, by careful adjustment of gas flow-rates. The success achieved in these trials suggested that this method of treatment of the coal was more likely to yield useful results than persistence with the previous technique. The necessary parts of the equipment were reconstructed and no further experiments were done in Series I.

XI. Experiments - Series II*

For the first few runs, no provision was made for a nitrogen supply to the collector at the base of the cyclone. However, appreciable deposition of tar and soot occurred, so the gas flow was introduced in order to prevent contamination of the coke and also to provide some cooling of the char particles.

After the initial trials, a screw feeder (Fig.16) was installed, to supply a continuous stream of coal to the apparatus; with a 60 rpm electric motor attached, the feedrate was about 10-15 gm/hr (depending upon particle size) and the equipment could be left running unattended for periods of 10-20 minutes. (Also see Plate 3.)

Stockton coal was used for the initial trials, but the old trouble of agglomeration was again experienced. Use of high gas rates reduced the problem somewhat, but satisfactory operation was not achieved until the swelling properties were destroyed by pre-oxidation of the coal (described later).

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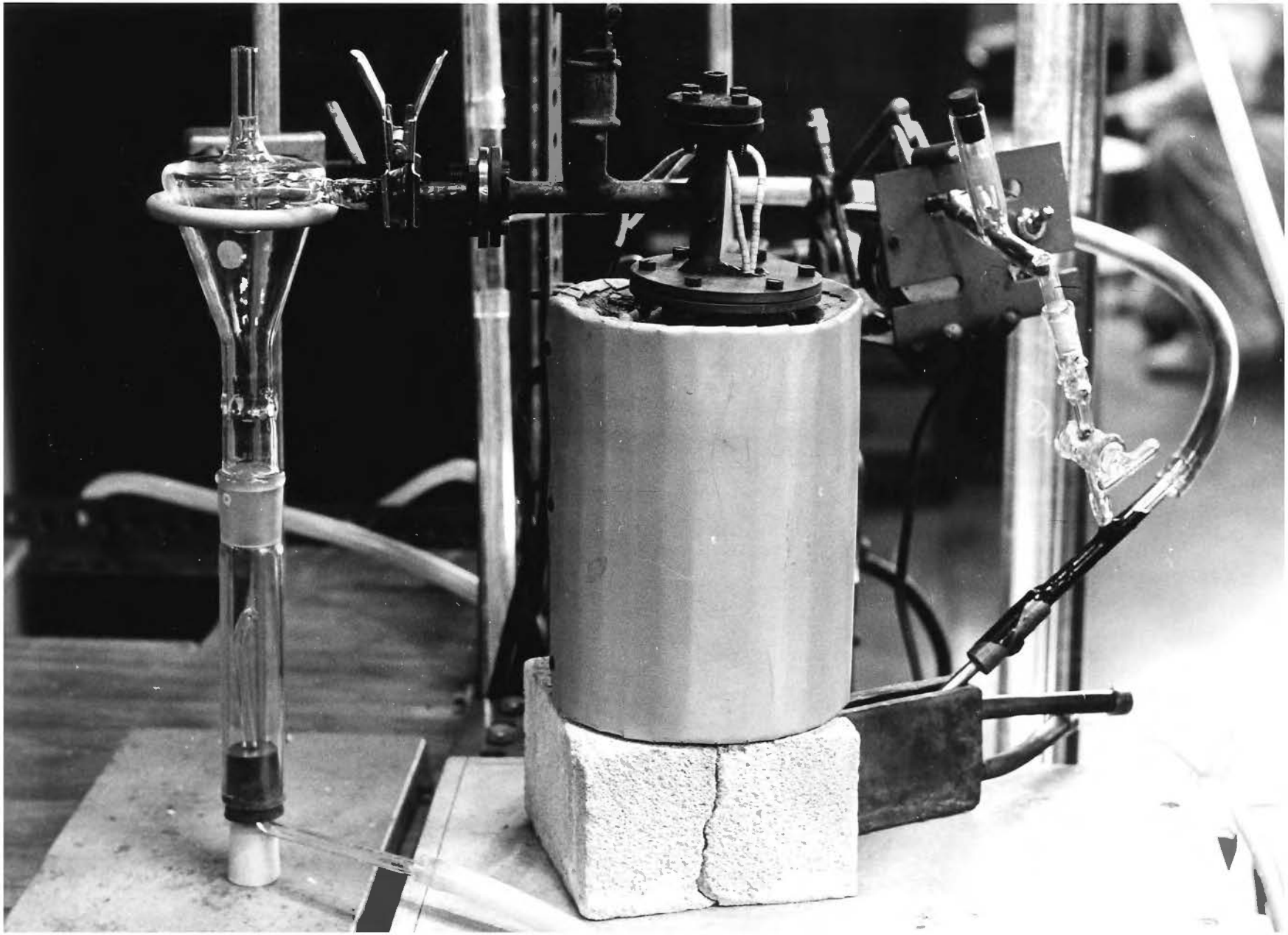
*It was discovered, some time after this series of experiments was completed, that Oxley[112] had used a similar method, in a study of the air/steam desulphurisation of high pyritic sulphur coals.



Wangaloa Coal

For the main series of experiments with this equipment, Wangaloa lignite was chosen, a high-sulphur non-coking coal, with which no trouble was experienced at any time.

Table 5

Properties of Wangaloa Coal (air dry basis)

Mesh Size	% total sulphur	% volatile matter	% moisture	% ash
60/72	4.24	56.4	14.8	4.42
85/100	4.39	56.1	14.1	4.91
100/120	4.42	56.6	13.4	4.77

As received, the coal was too wet for satisfactory operation of the screw feeder, so was air-dried for 24 hours in the laboratory. Initial runs used hydrogen as the gaseous atmosphere, but after run 174, nitrogen was used, being an inert gas, to eliminate any effects due to hydrogenation.

Results

Runs were made using three different coal particle sizes, but with no apparent difference in general behaviour. Fig. 17) (For detailed table of results, see Appendix.) The use of hydrogen (on 60/72 mesh coal only) shows no significant effect below 550^{o}C,

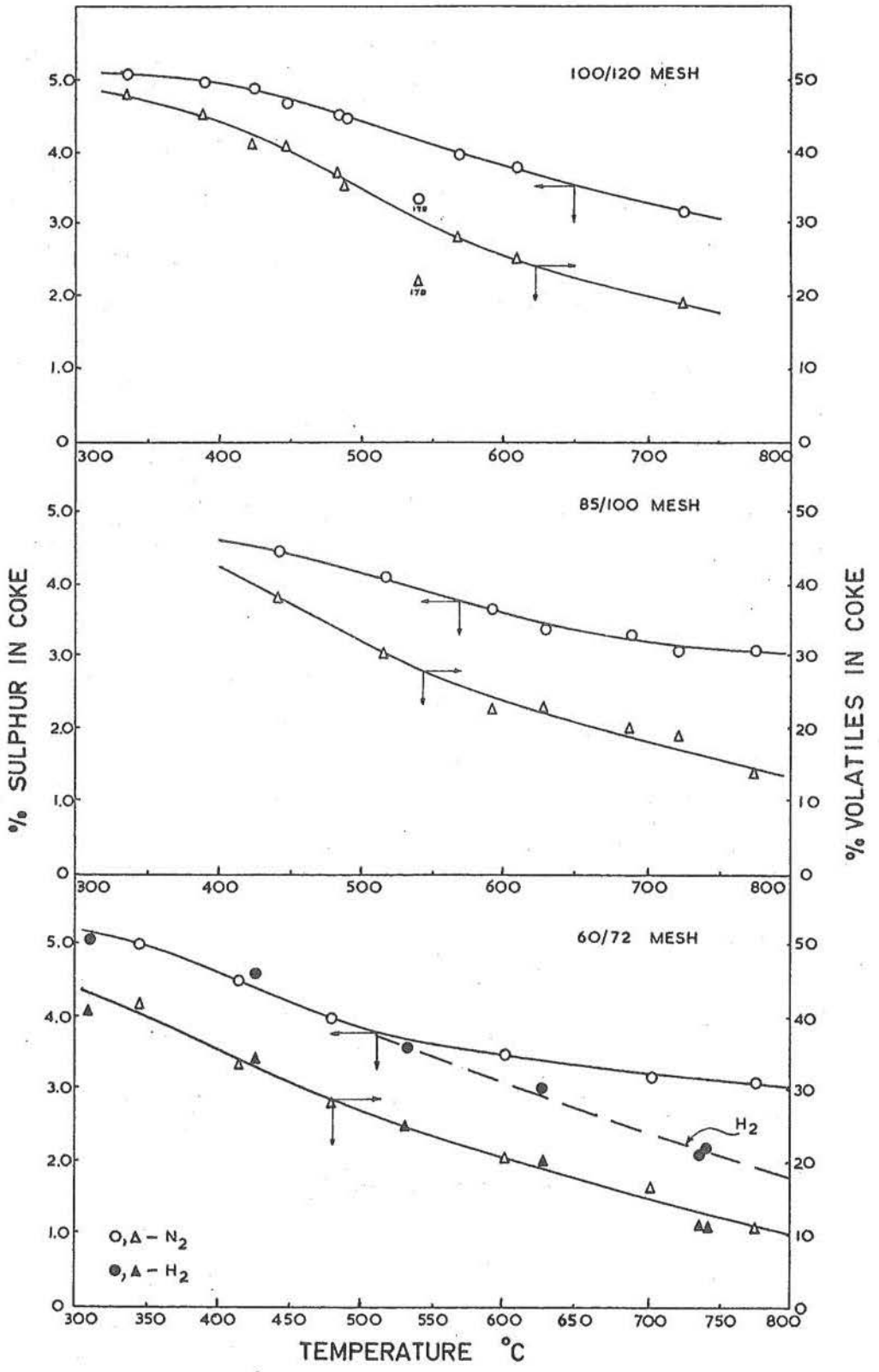


FIGURE 17 WANGALOA COALS: COMPOSITION OF CHARS AT DIFFERENT TEMPERATURES.

but above this temperature a gradually increasing desulphurisation will be noted. That this is probably due solely to the process of hydrogenation of the char sulphur is shown by the lack of any effect on the volatile content of the char.

It will be noted that the elimination of sulphur follows closely the loss of total volatile matter. To show more clearly the connection between losses of volatile matter and sulphur, the percentage loss of total sulphur was plotted versus the percentage loss of total organic (i.e. dry, ash-free) matter from the coal.

The percentage loss of total organic matter of a particular char sample was calculated by two different methods:

(a) Volatile matter basis, by using the percentage volatile matter of the char. According to Pitt[116], both Stone et al[139] and Chukhanov et al[14,31,130] incorrectly assumed that the percentage volatile matter of the reacting coal is linearly related to the proportion of the original volatile matter remaining in the coal. The correct expression for this calculation is

Percentage loss of organic matter

$$= 100 - 100 \frac{(100 - V_{coal})}{(100 - V_{char})}$$

where V_{coal} and V_{char} are the percentages of volatile

matter in the coal and char, respectively, determined according to the British Standard method.

(b) Ash basis, assuming the ash content of the coal to be conserved during the coking process, and thus provide a basis whereby the loss of organic matter can be determined. This appears to be just as realistic an assumption as that of the V.M. basis method, above.

Percentage loss of organic matter

$$= 100 - \frac{A_{coal}}{A_{char}} (100 - A_{char})$$

where A_{coal} and A_{char} are the percentages of ash in coal and char, respectively, again determined according to the British Standard method.

The percentage loss of total sulphur was evaluated by methods corresponding to assumptions (a) and (b) above:

Percentage loss of total sulphur (V.M. basis)

$$= \frac{S_{coal} - \frac{(100 - V_{coal})}{(100 - V_{char})} \times S_{char}}{S_{coal}} \times 100$$

Percentage loss of total sulphur (ash basis)

$$= \frac{S_{coal} - \frac{A_{coal}}{A_{char}} \left(1 - \frac{A_{char}}{100}\right) \times S_{char}}{S_{coal}} \times 100$$

(See Appendix for derivations of these formulae.)

It will be observed (Fig. 18) that a strong correlation exists between losses of total sulphur and total organic matter. A least-squares analysis of the data for runs in nitrogen gave the regression equations

$$S = 1.64\ V + 3.55 \quad \text{(V.M. basis)}$$

$$S = 1.33\ V + 1.06 \quad \text{(ash basis)}$$

(Correlation coefficients 0.99 in both cases, significance level $>$99.9%.)

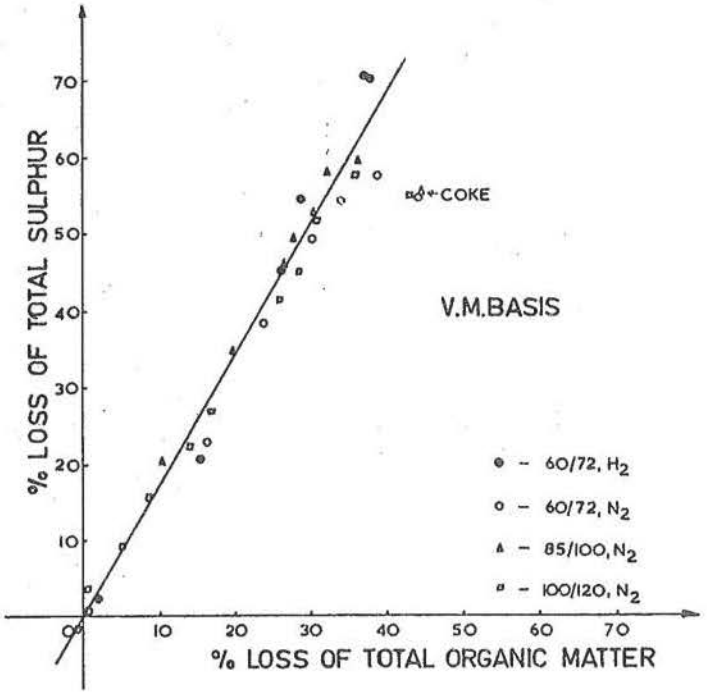
In order to provide a basis for evaluation of the effects of rapid coking, "cokes" prepared by a "conventional" (i.e. fixed bed) method were required. Since standard assay equipment was not readily available, samples were retained of the residues after treatment of the coal according to the Volatile Matter test procedure, at 925°C, and these were analysed for total sulphur and ash contents (Table 6).

Table 6

Properties of "Cokes" from Wangaloa Coals

	60/72 Mesh	85/100 Mesh	100/120 Mesh
Total Sulphur	3.85	3.85	3.91
% Ash	9.48	9.35	8.53

Volatile and Moisture contents zero, by definition. (Points corresponding to these data are labelled COKE in Fig. 18.)



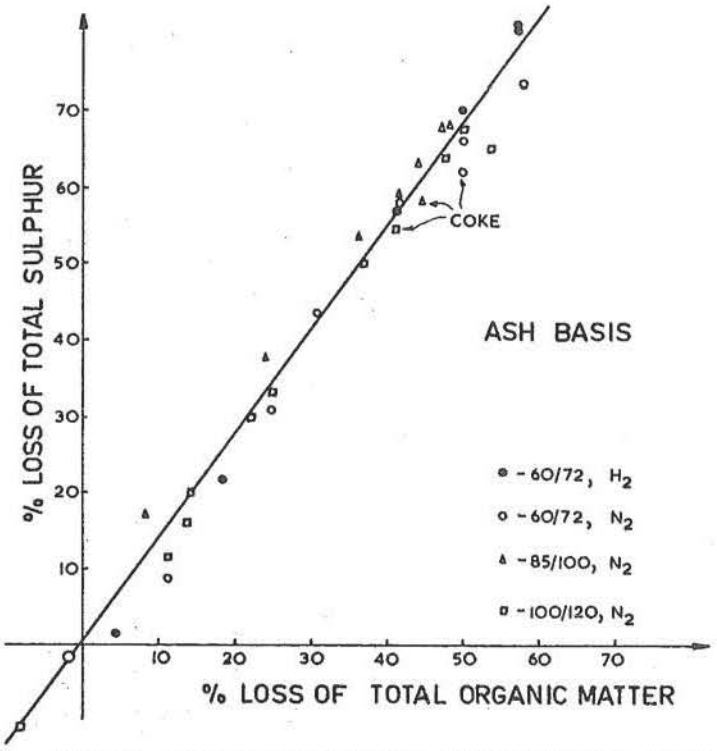


FIGURE 18 LOSSES OF SULPHUR AND TOTAL ORGANIC MATTER (V.M. AND ASH BASES)

Comparing the "Coke" results with the other points, on Fig. 18 (ash basis), it appears that the main effect of rapid coking is that a greater devolatilisation is possible. For Run 175 (at 780°C , the highest temperature reached in this series), the percentage loss of organic matter was 58.39%, compared with 50.44% for the "coke". Since the char from Run 175 still contained 12.83% volatile matter (by the B.S. test), further desulphurisation might well have been possible if even higher temperatures had been used.

Residence times of particles within the fluid bed varied according to temperature; at the lower temperatures it was difficult to obtain a precise estimate, but 20-30 seconds was taken as an average time, whereas at 700°C residence time was of the order of 3-4 seconds.. Since coal has an appreciably lower specific gravity than silicon carbide, and the coal particle sizes used were somewhat smaller than that of the bed material (about 40 mesh), it is to be expected that the coal, even in a cold fluid bed, will slowly elutriate. (As discussed by Levenspiel[92], the rate of elutriation of particles of a given size from a fluidised bed is proportional to the number of such particles present in the bed. Therefore, at a constant feed rate an equilibrium will be reached, at which the rate of loss of particles from the bed is

the same as the feed rate.) As the temperature rises, the probability of elutriation of a particle in a given time will be enhanced, due to the change in specific gravity of the coal, as volatilisation proceeds. At the higher temperatures, it is apparent from the residence time quoted above that the char spent little time in the bed, probably being blown almost directly from the injection tube into the outlet.

Tar in the exit gas stream tended to condense in the relatively cool outlet lines, with subsequent adhesion of char to the sticky deposits. Eventually, appreciable reduction of the cross-sectional area occurred, and the only effective way of removing the accumulation was to pass air through the apparatus, while playing the flame from a welding torch on the outside of the metal tubing.

Despite the success achieved with Wangaloa coal, it was felt that for this work to be of any value coking coals would have to be studied in the equipment. It was suggested by Dr J. B. Stott (who had by this time (early 1965) replaced Professor Siemon as supervisor of the project)that pre-oxidation of such coals, by destroying the swelling properties, might render them capable of being processed in the fluid bed without appreciably changing their basic composition.

Stockton Coal

A further series of runs was then made using Stockton coal that had been pre-oxidised for 24 hours at 150°C in the laboratory oven. The swelling number was thereby reduced to about 1 or 2, although a coke button was coherent, indicating that the coal still went through the molten state. This property is more effectively demonstrated by the microphotographs of coal and char particles in Plate 4. The char produced at 485°C shows incipient swelling; by 510°C the effect is complete, no further swelling being discernible in the char produced at 990°C. Oxidation for a further period of 24 hours at the same temperature made no noticeable difference to the swelling properties of this oxidised coal.

Table 7

Properties of Oxidised Stockton Coal (dry basis)

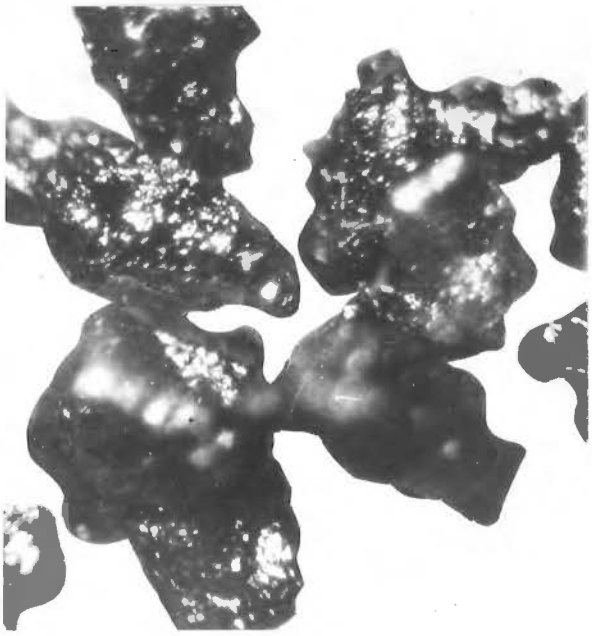
Mesh	% total sulphur	% volatile matter	% ash	Swelling number
60/72	1.22	33.4	0.1	1-2

Coke prepared according to the volatile matter test contained 1.23% total sulphur.

COAL

CHAR 485° C

CHAR 510°C



CHAR 990°C

Results

Behaviour of the equipment was not as good as with Wangaloa, but reasonable samples of char were obtained. Results are shown graphically in Fig. 19. A considerable scatter is apparent, due mainly to partial malfunctioning of the equipment.

During this series of runs, it was observed that char production did not occur at a constant rate during the course of an individual run. Typically, no product would be obtained for some minutes after the start of coal injection, a steady stream of char only appearing if the coal feed were stopped, or if the gas flowrates were appreciably increased. It was found possible to obtain a reasonable quantity of product only by operating with substantially increased gas flows, but at the expense of heavy contamination of the char by bed material.

The carborundum was separated from the char by a float-and-sink method; the sample was stirred vigorously into a beaker of water, and after settlement of the heavy carborundum, the top layer was decanted and the product filtered and dried at 105°C. This technique was not entirely successful in some cases, but in general only 1-2% of carborundum remained in the char. Where a greater quantity was found (Runs 203, 204, 216) the samples were rejected, since

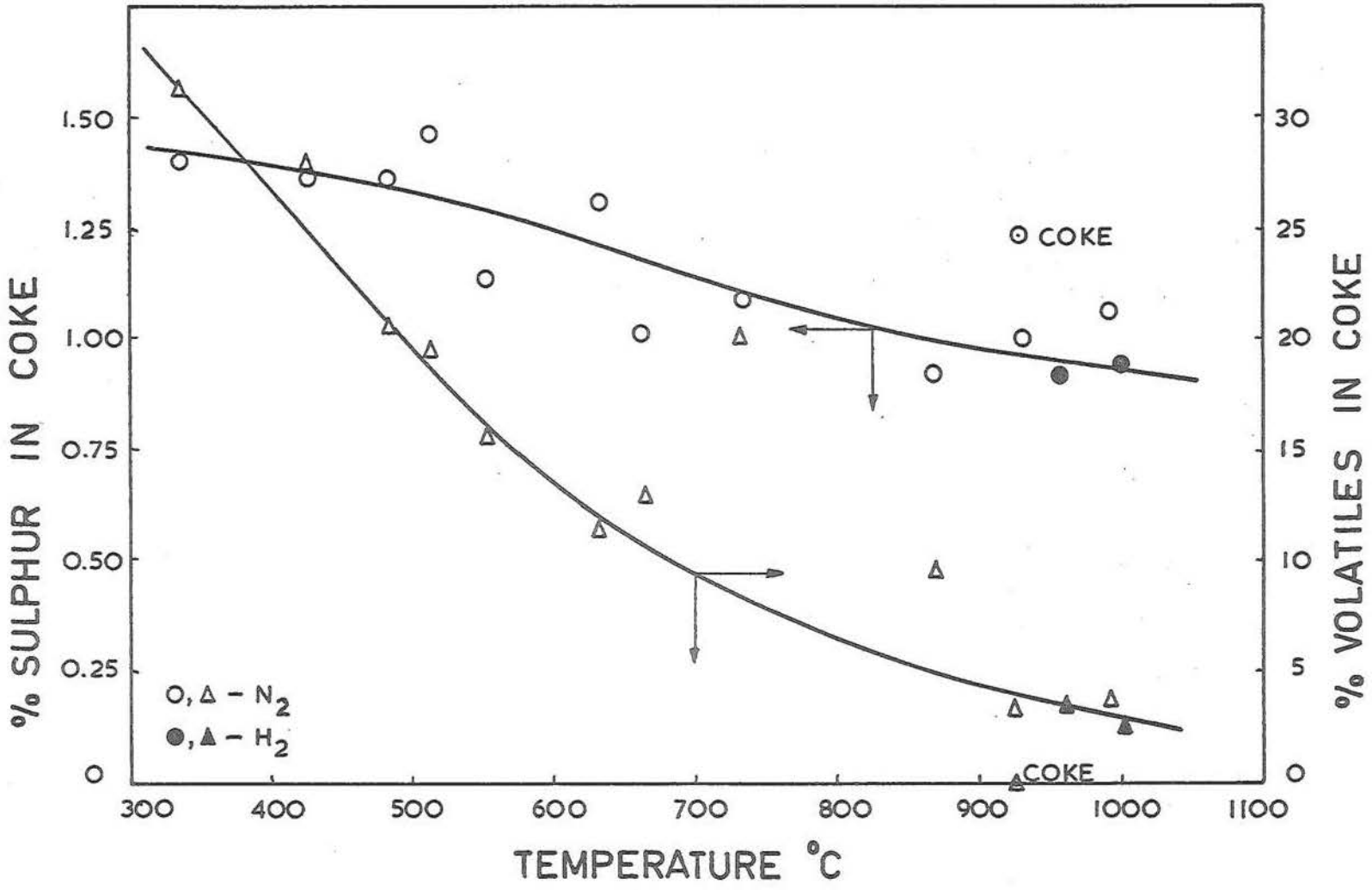


FIGURE 19 STOCKTON COAL: COMPOSITION OF CHARS AT DIFFERENT TEMPERATURES.

it was observed that an appreciable amount of carbon deposition had occurred on the carborundum. This would have had a small effect on the results of all analyses done on the product, even after correction of the quantity of char (by subtracting the weight of residual carborundum after ashing).

As a result of experiments with the top of the apparatus removed, it was found that, despite the low swelling properties of the oxidised coal, agglomeration of the bed was still occurring. It was only with the use of high gas flowrates that a product was obtainable, and this was due to the injected coal being forced through a channel in the agglomerated bed, directly into the outlet gas stream.

Due to this malfunctioning of the equipment little of a useful nature can be extracted from the results of the experiments on oxidised Stockton coal. Scatter in the results can be attributed to a number of factors, such as variation in residence times of particles in the apparatus, at different temperatures and gas flowrates, and the unknown extent of contamination of the product by carborundum, albeit present in small quantities.

For these reasons, and bearing in mind the necessity of studying coking coals under the conditions described in earlier sections of this report, it was

decided to abandon further attempts to treat coking coals in a fluid bed, and to make a fresh start with a vertical tube, disperse phase carbonisation apparatus.

At this point it is worth noting that, using this type of fluid bed apparatus, it is impossible to prevent contamination of the coke by the carbonisation products, due to their flowing cocurrently through the equipment. In addition, it was also found impossible to contain the particles within the fluid bed for a time sufficiently long for equilibrium devolatilisation to be attained. This condition was easily reached in the disperse phase equipment (see later).

XII. Experiments - Series III

To investigate the behaviour of this type of equipment, two small tube furnaces (12" and 16" long, respectively) were modified, as shown in Fig. 20, to permit continuous processing of coal in an inert atmosphere at very short heating times.

Charming Creek Coal

The coal selected for the initial stage of this study was from the Charming Creek mine, a high-swelling high-organic-sulphur coal. For the first runs (up to number 230), an old sample of the coal was used, total sulphur 5.50%. For all others, a newer sample was obtained,of higher sulphur content, but otherwise identical specification (Table 8).

Table 8

Properties of Charming Creek Coal (air-dry basis)

Mesh size	% volatile matter	% ash	% moisture	B.S. Swelling number
35/100	46.9	3.11	1.93	8 - 9

Forms of Sulphur

% total sulphur	% organic sulphur	% pyritic sulphur	% sulphate sulphur
6.43	5.87	0.56	<0.01

"Coke" from the Volatile Matter test contained 5.20% total sulphur, and 7.13% ash.

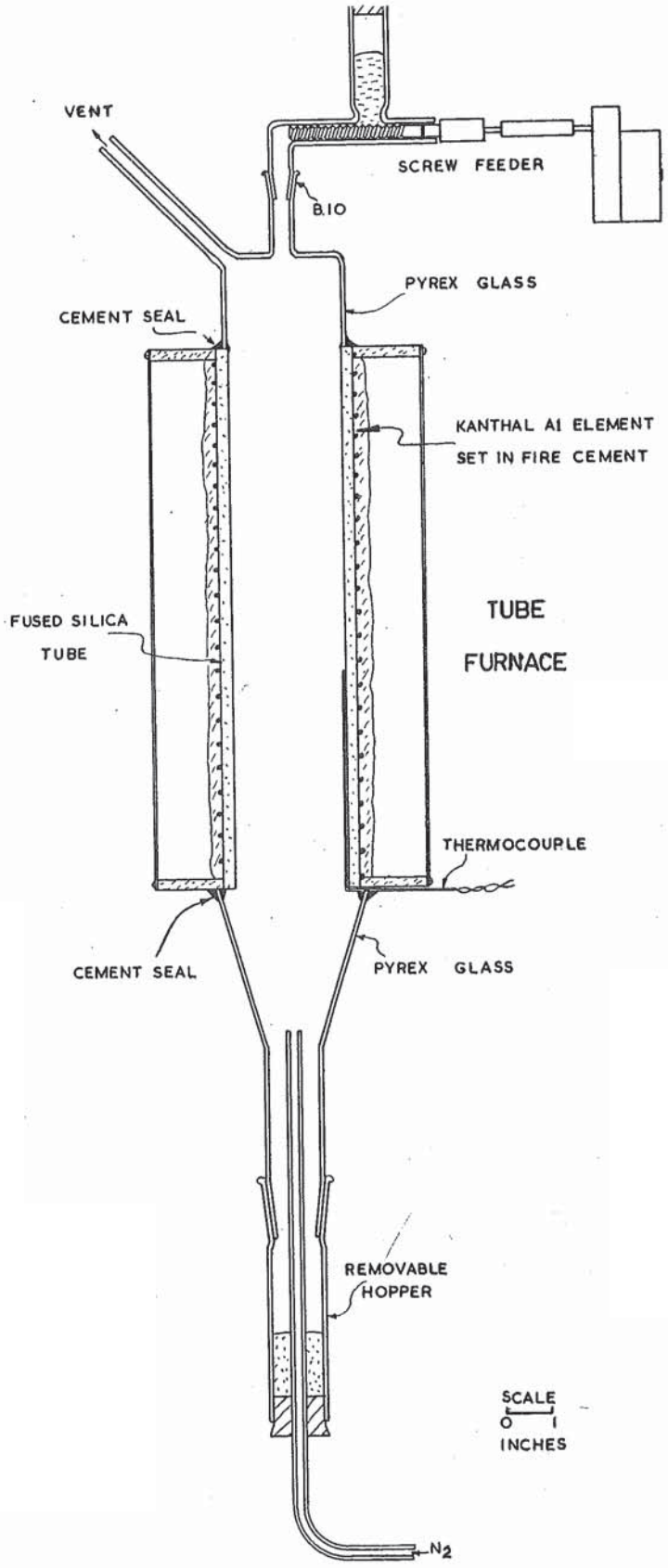


FIGURE 20 DISPERSE PHASE CARBONISATION EQUIPMENT, AS USED FOR INITIAL RUNS.

Experimental Work

Initial experiments were made with the screw feeder described in the previous section, but the results of the first run (220) indicated that the feedrate was too high. During the run, smoke completely filled the equipment, and the product was a mixture of coked and uncoked material, swollen to widely varying extents.

This was almost certainly due to particles close to the walls of the tube being subjected to far greater radiant heat transfer than those at the centre of the tube, and to local cooling of the hot gas stream by the first wave of carbonising particles. For this reason, a new motor (10 rpm) was obtained for the screw feeder, delivering only about 2 gm/hr of coal.*

*It is interesting to note here that Snow[93] (op cit p. 54) in equipment of similar diameter, used a coal feedrate of 130 gm/hr, and gas flowrates comparable with those in the present series of experiments. From the behaviour noted above, it is apparent that the improvement in desulphurisation noted by Snow, due to increase in hydrogen flowrate, is just as likely to be due to reduction in smoke concentration (giving better heat transfer) as to any effect of hydrogenation.

It is also worth noting that, in the experiments of Chukhanov et al[78] (op cit), the procedure used was that of dropping a 1 gm sample of coal down the heated tube, all at once. It appears that, contrary to the assumption of these authors, their coal sample would not be uniformly heated during passage down the tube.

With this modification, the rate of smoke generation was sufficiently low for it to be rapidly dispersed by a gentle stream of nitrogen, and the coke was of a uniform quality, apart from the presence of a fine white powder. It was found that this was due to leakage of air into the apparatus, and partial combustion of the coal particles. The leaks were sealed by filling cracks in the furnace tube with fire cement and painting with sodium silicate solution.

From visual observation, the residence time of particles in this tube was found to be about 1.5 seconds, at all temperatures. Individual particles did not have the same time of passage - due to turbulence in the gas flow within the furnace - but all came through within 1 to 2 seconds. It was not possible to change this residence time significantly by varying the flowrate of the countercurrent stream of nitrogen because at higher flows most of the coke was elutriated, and at lower flows the tube rapidly filled with smoke. Another point is that, at high gas flowrates, the gas is not heated sufficiently rapidly, to the temperature of the walls of the tube, and hence disturbs the temperature pattern within the furnace.

A short experiment was conducted to determine whether the gas flow used (1 litre/min) had any great

effect on the temperature at the centre of the tube by suspending a thermocouple from the top of the apparatus, at various levels, and comparing its readings with those from the main thermocouple cemented to the wall of the tube. The thermocouple was moved from the bottom to the top of the furnace and it was found that, over the temperature range of interest, the maximum discrepancy was $10^{o}C$. For all subsequent runs, the directly measured temperature was used without corrections.*

However, it is highly probable that the coal particles did not reach the wall temperature until coking was fairly close to completion, due to the heat demand of the process. It was hoped that this source of error would be minimised by using particles sufficiently small for the heating time to be small, compared with the residence time within the tube.

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*In this context, note that it is possible[103] to measure the temperature of particles in such an apparatus as this by photographing them with colour film, and comparing the colour of the glowing particles with those of a series of tungsten ribbons, heated to known colour temperatures. For particles at temperatures lower than that at which light emission occurs, a similar technique using infra-red sensitive film might be feasible. The presence of smoke might, however, introduce difficulties.

Analysis of the chars produced at a number of different temperatures in both nitrogen and hydrogen showed that desulphurisation and devolatilisation were considerable, even though the residence time was so short.

A new furnace was constructed on a 4 ft long by 2½ inch diameter fused quartz tube, but even in the absence of cracks in the furnace liner it was still impossible to be sure that all leaks were eliminated. For this reason, an Incoloy DS tube was fabricated (Figs 21 and 22) to fit inside the furnace and ensure that the apparatus was gas-tight. (When tested with a rotary vacuum pump, a vacuum of about 29.9 inches of mercury could easily be maintained.) All runs subsequent to 251 in this series were made either in this equipment or a slight modification, in which the single 4 ft long tube furnace was replaced by a stack of three 15 inch furnaces. The latter arrangement was to enable kinetic data to be obtained; by using one, two, or all three furnaces at a time, three different carbonisation times could be obtained at any temperature of operation. After Run 343, five such furnaces were installed (Plate 5).

By using the small modification shown in Fig. 22, it was possible to do a short series of runs under vacuum to determine whether any appreciable effect would be observed. Residence times for the coal particles were only of the order of 0.5 second, due to the absence

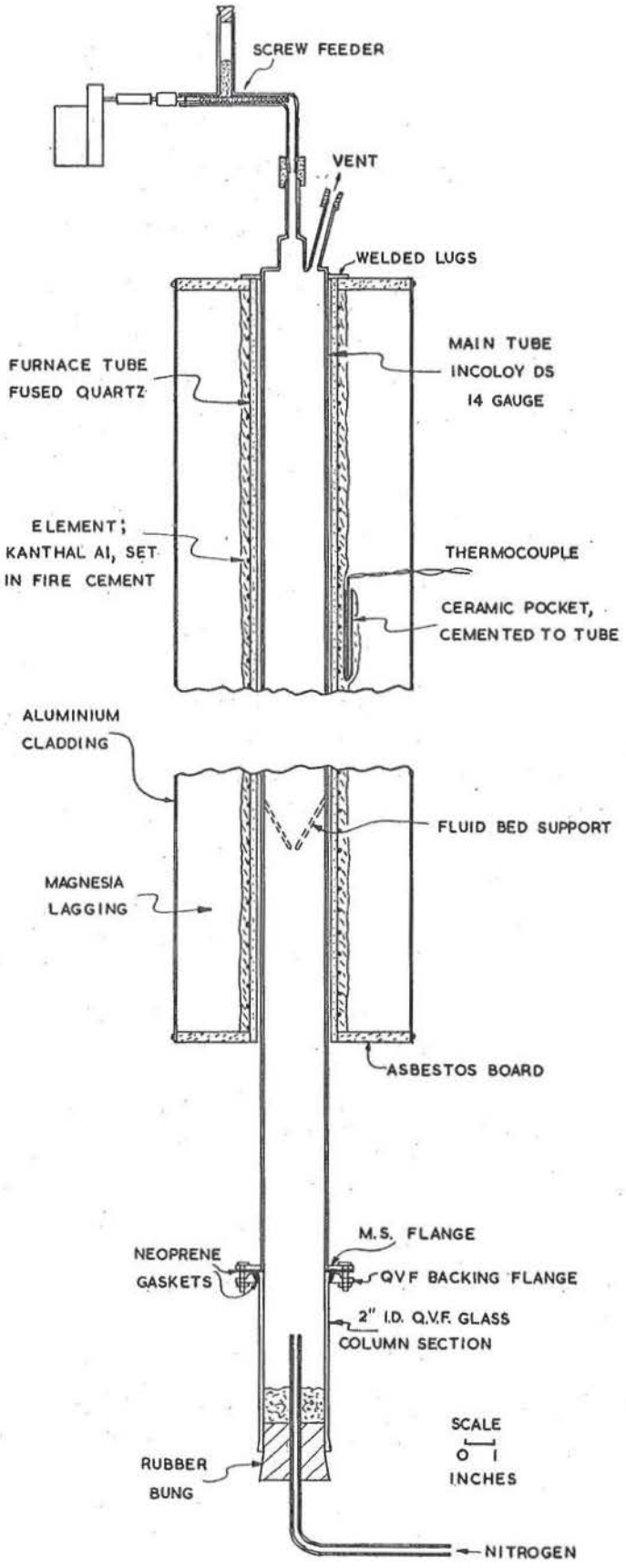


FIGURE 21 INCOLOY DS INNER TUBE AND 4ft TUBE FURNACE, AS USED FOR MAIN RUNS (SERIES III)

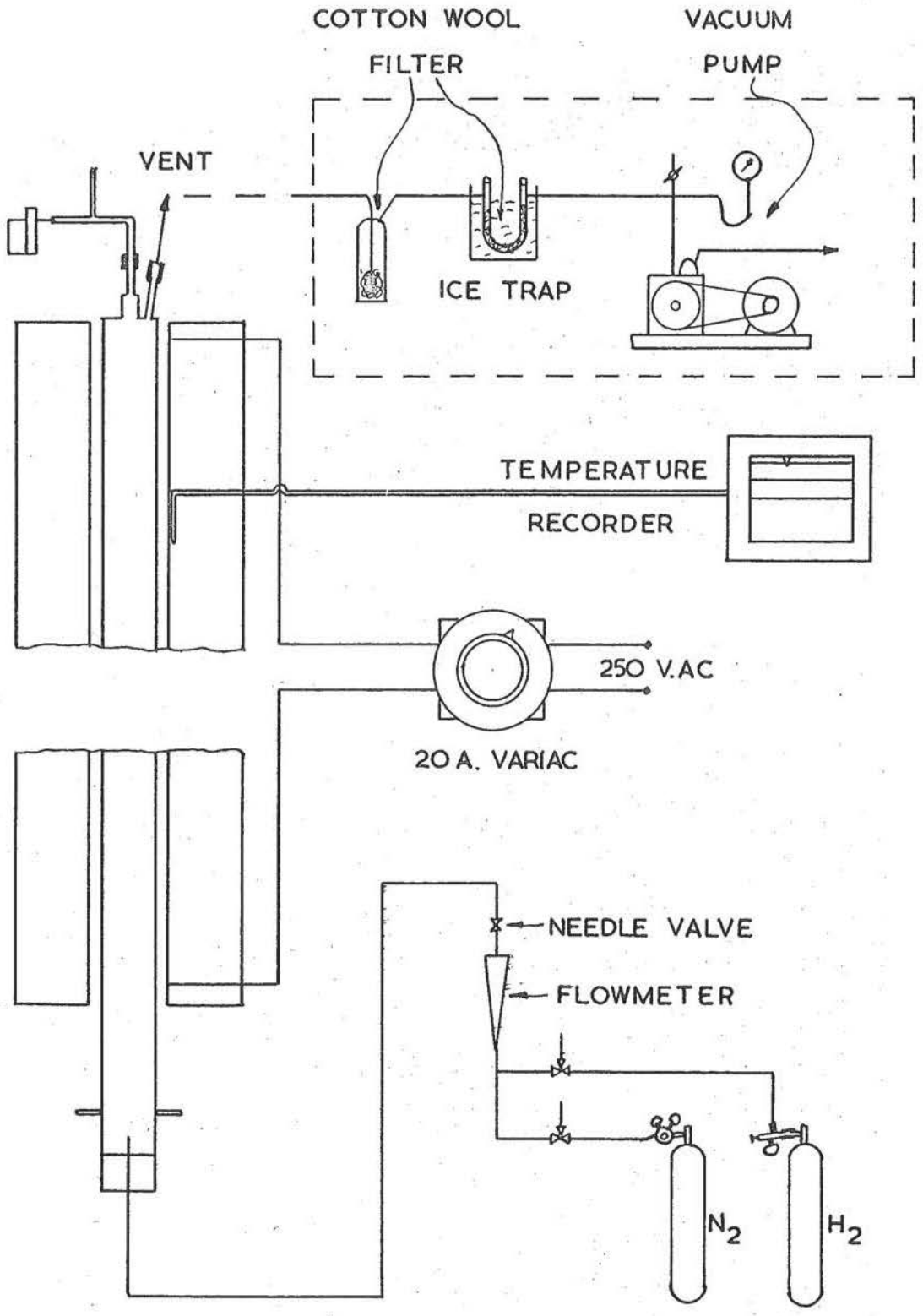
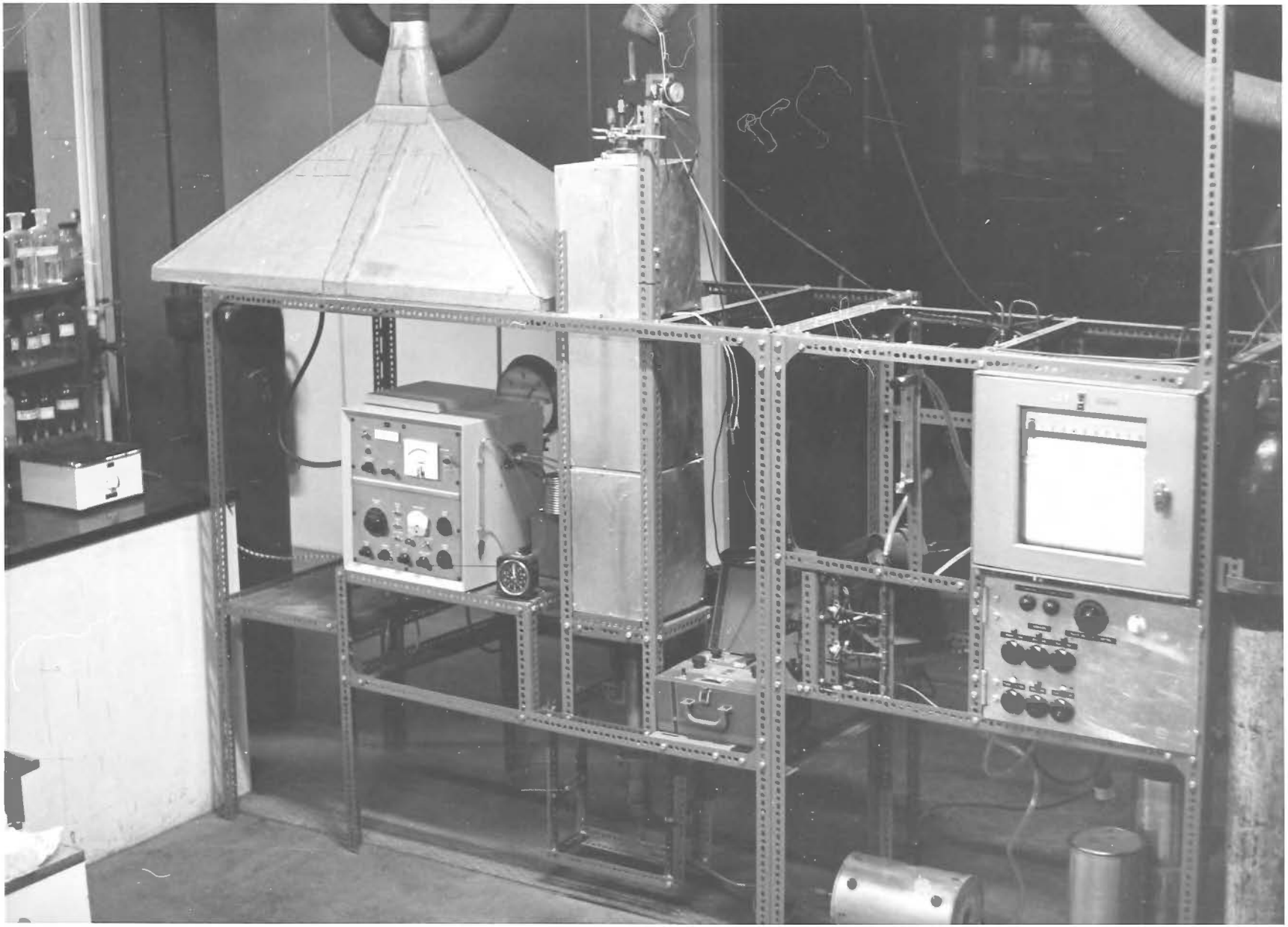


FIGURE 22 SCHEMATIC DIAGRAM OF EQUIPMENT AND SERVICES, INCLUDING MODIFICATIONS FOR VACUUM RUNS.



of aerodynamic drag, but decomposition was still appreciable at the highest temperature used, 1005°C. The vacuum during these runs varied between 28.0 and 29.5 inches of mercury.

To obtain data on the composition of the chars at "equilibrium" (i.e. after a sufficiently long time at the carbonising temperature for decomposition to be virtually complete) a constriction was welded into the Inconel tube, as shown in Fig. 21. This comprised a 60° inverted cone, with a 3/16 inch hole drilled through the apex. The flow of nitrogen through the column was such that the char particles formed a fluid bed (more correctly, a spouted bed) above this constriction, and could thus be retained for as long a time as necessary. By shutting off the flow of nitrogen, the particles could pour through the hole in the base of the cone and be collected in the usual manner.

(In the opinion of the writer, this is a better system than that of Chukhanov (op cit), in that it permits the particles of char to finish carbonisation under conditions such that gaseous products are rapidly flushed away; in Chukhanov's equipment the char was collected in a cup within the furnace, and the process completed in a local stagnant atmosphere of carbonisation products.)

The normal operating procedure in these experiments

was to run the coal feed for about 30-40 minutes, shut off the feed for about 5 minutes (to ensure that the last-injected particles had finished carbonisation), then stop the gas flow and collect the sample. (According to the results of Chukhanov, carbonisation in this type of equipment is virtually complete after 5 minutes.)

It was not found possible to collect the product from carbonisation at 500°C, due to the coal still being in the molten state when it reached the constriction. The resultant mass of char rapidly blocked the hole, and had to be burnt out by passing air through the tube.

Following the encouraging results obtained from the hydrogenation of Wangaloa coal, experiments were carried out to determine the effects of hydrogenation on the "equilibrium" char described above. The procedure was to prepare char in the "fluid bed" as before, then change the gas flow from nitrogen to hydrogen for a measured period. The hydrogen was then flushed from the system before collection of the char as already described.

A great deal of trouble was experienced in obtaining reproducible results from these runs. It was apparent from the variation in ash contents that losses by combustion were still occurring. The source of oxygen was eventually located; "commercial" nitrogen cannot be relied upon to be better than at best 99.5% pure. The

remaining 0.5% is mainly oxygen, and at the flowrates used was capable of causing losses of up to about 0.1 gm of carbon per hour, as carbon monoxide. This is an appreciable proportion of the production rate of char from the equipment (about 1 gm per hour).

Since "oxygen-free" nitrogen was not readily available, the commercial gas was purified by passing through an Incoloy DS tube,packed with copper turnings, at a bright red heat.

The "straight-through" runs were not repeated, using this purer nitrogen, since it was thought that the residence time of char in the apparatus was too short and the oxygen partial pressure too low for a significant amount of combustion to occur. (As has been emphasised by Essenhigh[52], in his studies on the combustion of fine coal, it is not until the initial stages of coking are near completion that combustion of the solid material starts. This is because the combustion flame front is initially located in the boundary layer of volatile carbonisation products; combustion of the solid residue occurs later in the process.) For this reason, it was concluded that little, if any, error would have been introduced by the use of less pure nitrogen in these runs.

Another factor that caused trouble in the early runs was the presence of inhomogeneities in the coal;

no special precautions had been taken during grinding and screening to ensure that the coal was well mixed, and it was later found that the ash content of coal from separate sample containers varied by as much as a factor of two. For all main runs, the sample was carefully mixed, and stored in a single, large container.

A further interfering factor in these early runs, and to a lesser extent in all subsequent runs, was contamination of the product by scale from the Incoloy tube. In the runs at 1005°C, the alloy was being subjected to conditions sufficiently severe for slight scaling to be present, despite the fact that 99% of the time was spent in an inert atmosphere. Scale could easily be detected by microscopic examination of the ash, so all samples containing more than a minute quantity were rejected. However, it was found that, provided the tube was not tapped or otherwise mechanically agitated during a run, significant contamination by scale did not occur.

During most runs appreciable quantities of char stuck to the sides of the tube (especially at the top where temperatures were low enough for tar to condense), in some cases to such an extent that a cake of up to a quarter-inch thick was formed. The only way to remove this deposit was to burn it off at the end of a run by allowing air to pass up the tube, while heating

the top section of the tube with an oxy-acetylene flame.

Estimation of Loss of Weight During Carbonisation

In spite of the above-mentioned precautions, no detailed results emerged from the experiments on Charming Creek coal; a number of approaches was tried, but no means was found whereby the loss of total organic matter could be estimated reliably. Methods tried were as follows:

Weighing of feed coal and product char, to obtain a direct measurement of the quantity of organic material lost during carbonisation. This method was not successful, mainly due to the extreme caking properties of Charming Creek coal, which resulted in a build-up of char on the walls of the furnace. Lowering the gas flowrate reduced this problem slightly, probably by virtue of its effect on gas turbulence, but even so the best results obtained were not reproducible enough for use (e.g. four replicate determinations (Run 240) gave char recoveries of 21, 23.5, 27 and 28% of the coal injected). It was found later that when using non-swelling or low-swelling coals, this problem did not arise to a significant extent; such coals were used in the final series of experiments, described later in this report.

Volatile matter basis, as used in Series II

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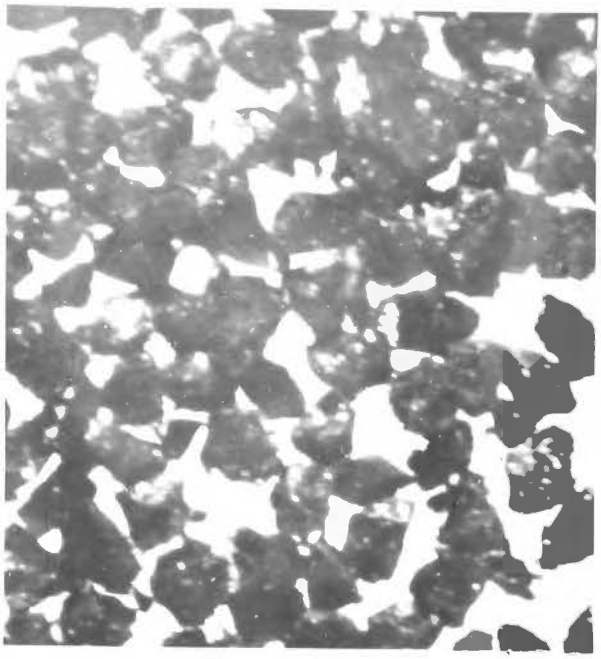
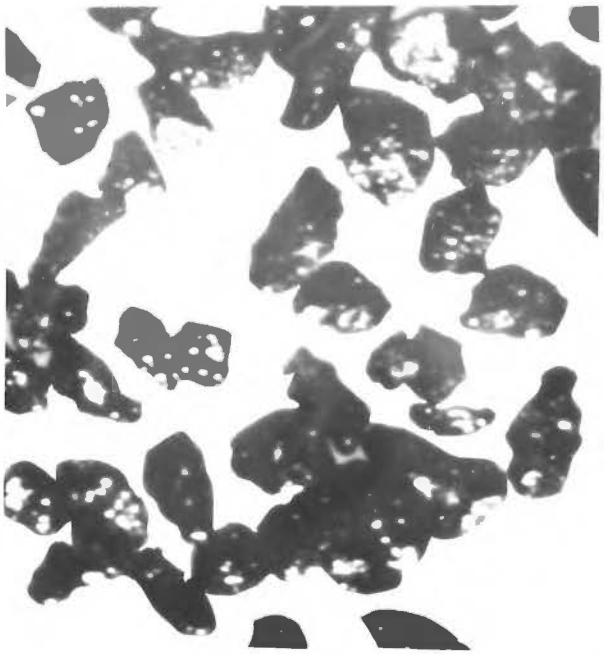
experiments. This could only be applied to the "straight-through" runs, since the extent of devolatilisation in the equipment was so great in the "equilibrium" runs at other than the lowest temperatures used that very little volatile matter remained. The difficulty of obtaining meaningful results from this standard test was enhanced by the fact that, due to the very low specific gravity of the highly swollen particles of char (see Plate 6), the test crucibles could only hold about 0.2-0.3 gm of material, instead of the 1 gm required by the test procedure. Results obtained (see table of results, Appendix) were frequently inconsistent with the conditions of formation of the char, and for this reason the V.M. basis method was only applied up to Run 255.

Ash basis, as used in Series II. Results of ash determinations were not useful in that (see table of results, Appendix) in most cases an increase in carbonisation time appeared to give rise to a reduction in ash content, although this general trend was subject to appreciable scatter. Three reasons may be put forward to explain these results.

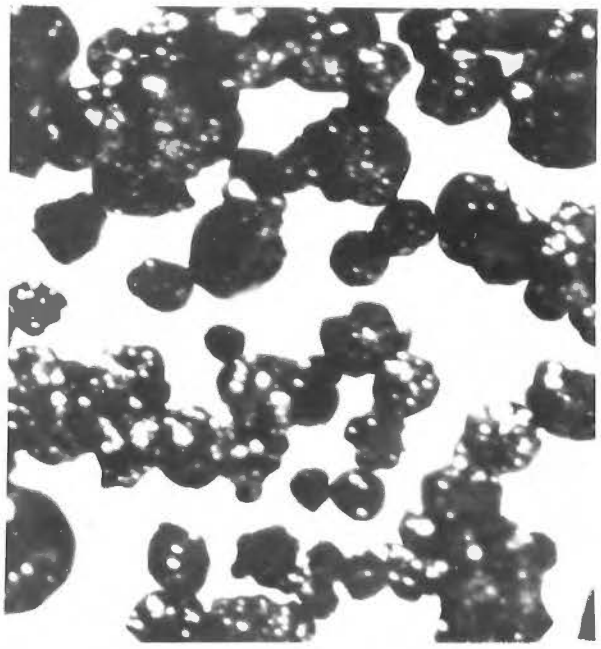
(i) The mineral matter of coal is affected by the temperatures involved in carbonisation, as is the volatility of the sulphur retained in the solid residue, thus affecting the composition of the ash residue and



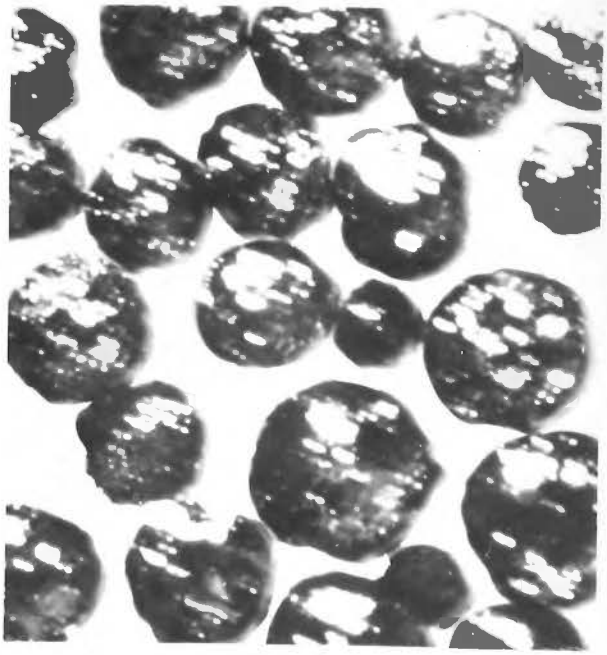
COAL



CHAR 500°C



CHAR 620°C



CHAR 1005°C

the fixation of sulphur by the ash[149]. This suggested mechanism is supported by the differences noted in physical appearance of the ash obtained from the coal, and from chars prepared at different temperatures.

(ii) Loss of ash during the ashing process. The possibility of such a loss will be apparent when it is stated that when highly swollen chars were ashed, the result was a very light, fluffy residue. Great care in handling was required to prevent the ash from blowing away in light air currents. This suggested mechanism is supported, to some extent, by the discovery that reproducible results were not obtainable when duplicate samples of coal were ashed, and the ashes analysed spectrochemically for iron and silica, according to B.S. 1016. It is important to note, here, that replicate analyses of the same sample of ash gave much more closely reproducible values; this implies that the analytical method is reliable.

(iii) It was noted during operation of the equipment that small quantities of char were continually being elutriated, via the vent. This was mainly confined to small particles (probably produced by the slight grinding action of the screw feeder) and although very low countercurrent gas flowrates were tried, it was not found possible to eliminate this loss entirely. In view of the lack of consistency of the results, it is

not unlikely that the fraction of product lost by elutriation may have affected the composition of that which was collected and analysed.

It is difficult to know which, if any, of the suggested mechanisms (i), (ii) and (iii) is the most important. An investigation of (i) and (ii) would probably show valuable results; (iii) could probably be reduced by redesign of the apparatus, possibly by using cocurrent flow of coal and gas.

Analysis for Iron and Silica

Attempts were made to analyse the char ashes for iron and silica, in the hope that these would provide an invariant basis for estimation of organic matter losses. No useful information was obtained, probably for the reasons given in (c) (ii) and (iii) above. (For results, see Appendix.)

Weighing of Char Particles

The fifth method used was to obtain an average value for the weight of an individual char particle, and attempt to relate this to the coal particle weight. The procedure involved weighing a small number of char particles (on the Chemistry Department's Cahn

Electrobalance, sensitive to 0.1 microgram) and then counting under a stereo-microscope. Appreciable difficulties were introduced by the presence of large quantities of fine particles in many samples. This was probably due to the slight grinding action of the screw feeder; from the appearance of some particles, it is also probable that the almost explosive swelling in the initial stages of carbonisation caused rupture and fragmentation of the char. The former effect was probably the cause of an inability to obtain consistent results, even from repeat determinations of the coal itself (after being through the screw feeder). As an example, six replicate determinations gave between 3.3 and 4.3 for the weight in micrograms of a coal particle, and five determinations on an apparently uniform sample of char (Run 295) gave from 2.1 to 2.8 micrograms; more obviously non-uniform samples showed appreciably greater scatter.

Results

For the initial "straight-through" runs (numbers 227-255) it was possible, as mentioned previously, to evaluate losses of sulphur and volatile matter by the volatile matter method developed in the experiments on Wangaloa coal. Results of these runs are shown

in Fig. 23 (a), and show that, despite a fair amount of scatter (attributable to differences in the types of process used in the various sets of runs, as well as to the sources of variation outlined above), a strong linear relationship exists between sulphur and total organic matter losses. The regression equation is

$$S = 1.91\ V + 4.60$$

(Correlation coefficient 0.93, significance level $>99.9\%$.)

This result is, however, not entirely reliable; for the reasons already given, the chars may not have been representative samples.

As a consequence of the difficulties outlined above, it was necessary to repeat each run two or three times, after each set of difficulties had been ironed out. The results shown in Fig. 23 (b) are from the final group of runs, numbers 312 to 339, and serve to compare the "straight-through" and "equilibrium" runs.

Main Runs

Fig. 23 (b) shows the change in total sulphur content with different decomposition times, up to "equilibrium". It is apparent that sulphur

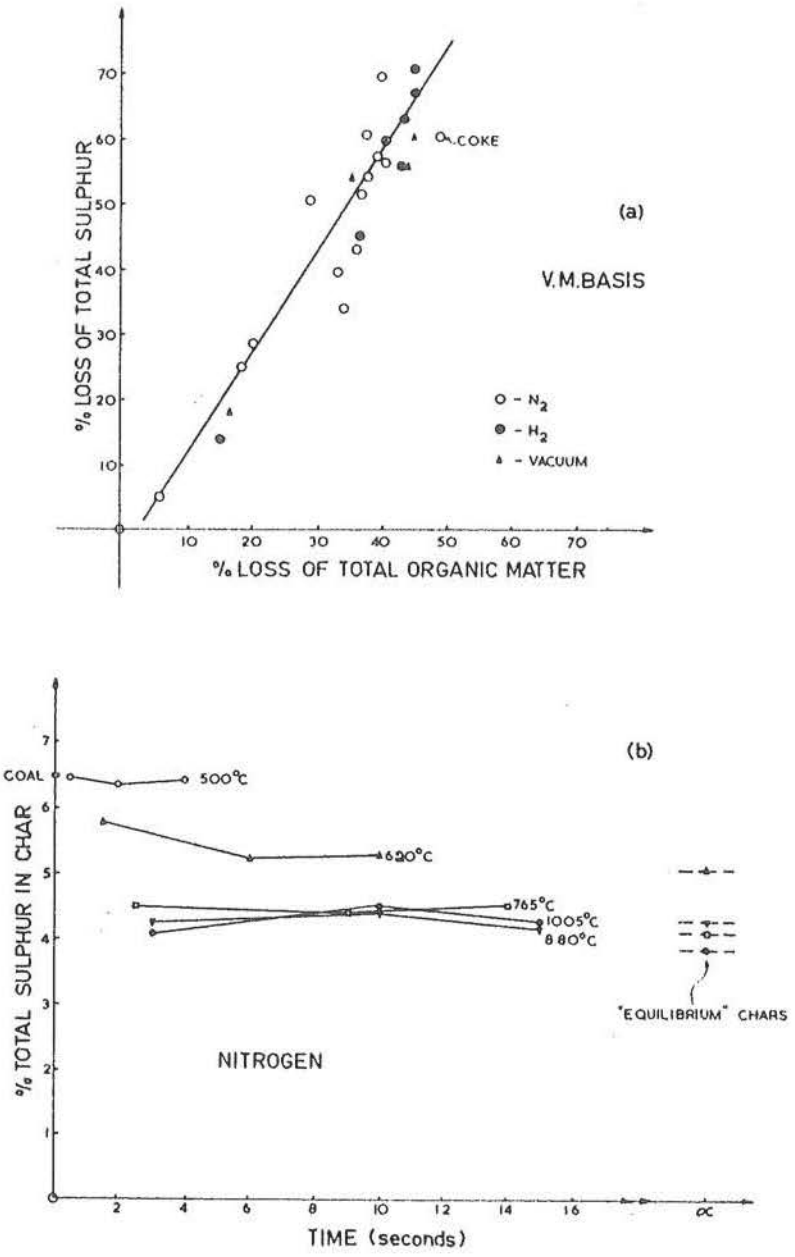


FIGURE 23 CHARMING CREEK COAL: (a) SULPHUR AND TOTAL ORGANIC MATTER LOSSES (V.M. BASIS)
(b) VARIATION OF SULPHUR CONTENT WITH CARBONISATION TIME AND TEMPERATURE.

volatilisation proceeded at a greater rate than that of total volatile evolution, during the first 1-2 seconds, but thereafter either volatilisation was virtually complete or else sulphur loss was proportional to total organic matter loss, the sulphur content thereby remaining fairly constant.

It is interesting to note that, at the three higher temperatures, there is little significant difference in behaviour. This result may support the claim of Trifonov[146] (op cit) that the organic sulphur fixation process is complete at a relatively low temperature.

Vacuum Operation

Results of vacuum operation (Fig. 24(a)) are not comparable with those in nitrogen, due to the appreciably shorter residence time within the heated tube (0.5 seconds for all runs). However, the graph shows an interesting trend, in that the sulphur content of the char decreases, up to 750-800°C, and then increases again at higher temperatures. Whether this can be attributed to the effects of operation under vacuum, or merely to the result of an earlier stage of decomposition is not known.

It was noted that appreciably more tar was

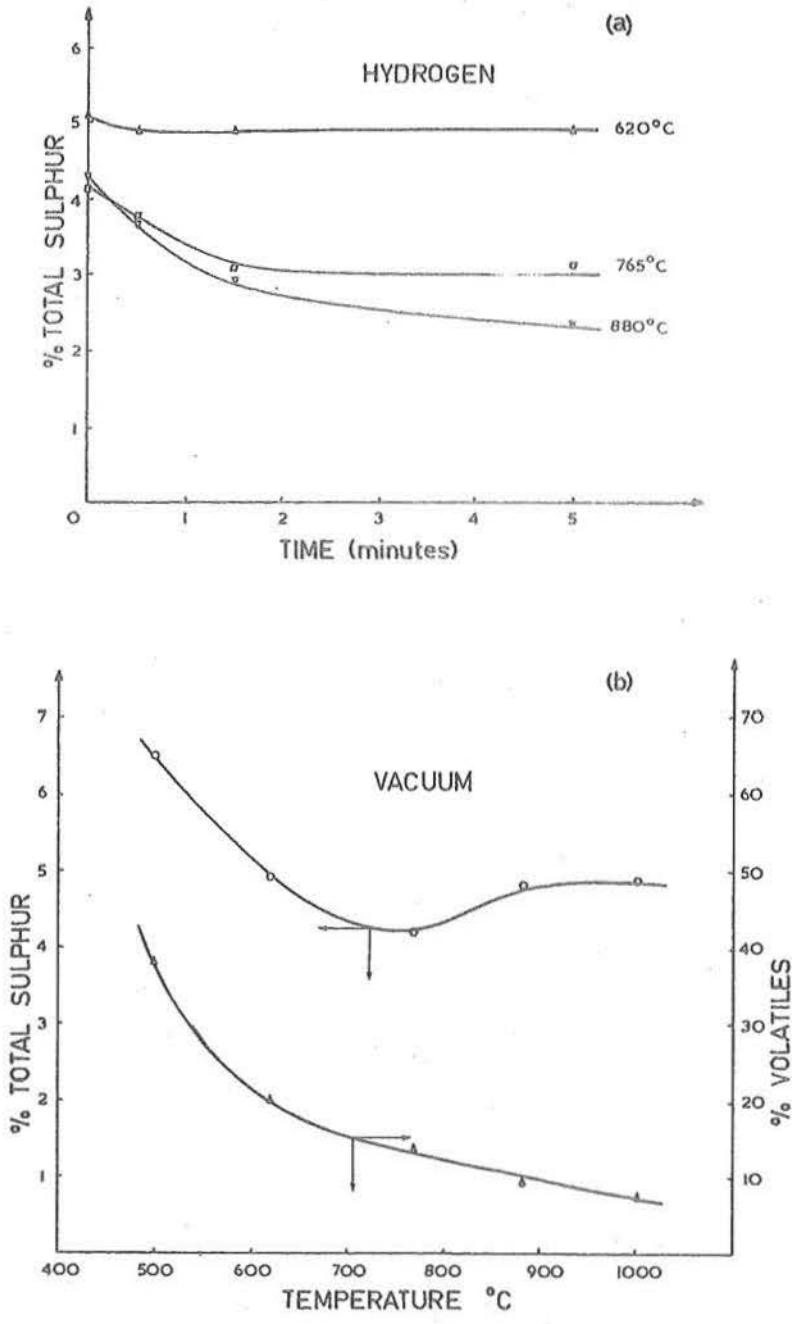


FIGURE 24 VARIATION OF SULPHUR CONTENT WITH (a) HYDROGENATION AND (b) CARBONISATION UNDER VACUUM.

produced, than from the runs in nitrogen; also, that a fine, unpleasant-smelling brown powder was carried through to the filter at all temperatures. In the absence of hot gas, and with the short residence time of volatile products within the furnace, it is likely that vapour-phase thermal cracking of the primary decomposition products was inhibited, thus producing increased quantities of tar. The brown powder may compromise high molecular weight fragments from the coal surface as has been suggested by Yellow[160] (op cit).*

Hydrogenation

Hydrogenation of the "equilibrium" char (Fig. 24(b)) showed an initial, rapid decrease in sulphur content, but after 1.5 minutes, little effect was apparent, except at the higher temperatures. This result tends to support the conclusion of Zielke et al[161] (op cit) and Fig. 3(a), that sulphur is preferentially removed in the initial stages of hydrogenation, but that the rate of sulphur loss soon decreases, to such an extent

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*Vacuum carbonisation may well be a useful means whereby the primary devolatilisation products may be studied with the minimum of degradation by thermal cracking. The subject is worthy of further study.

that the sulphur content of the char remains approximately constant, as carbon gasification proceeds.

If it can be assumed that the sulphur contents of the chars were representative, the main conclusion to be drawn from this work on Charming Creek coal is that the majority of sulphur emission occurs during the initial stages (maximum 2 seconds) of carbonisation. This conclusion is apparently at variance with that reached by Chukhanov[30] and Kaliuzhnyi[82] (op cit), who stated that the initial liberation of sulphur is small, the main products being given off in the second decomposition stage, from 0.1 second up to 2-3 minutes. However, as discussed earlier, the division of Chukhanov's results into three arbitrary stages is not entirely justifiable; in any case, the duration of the second stage appears to be too long for results to be usefully described by only one kinetic equation.

Wangaloa and Dauntless Coals

Experimental Work

As stated earlier, the main difficulties in the quantitative estimation of loss of weight of Charming Creek coal arose from its extreme swelling properties; much char was lost via the gas outlet, and accumulation of coke on the inside of the tube was considerable.

It was reasoned that, by using non-swelling or low-swelling coals, these difficulties would not occur to an appreciable extent; such was found to be the case. Table 9 gives the properties of the two coals used in these runs (see Appendix for Table of Results).

Table 9

Properties of Wangaloa and Dauntless Coals (dry basis)

Coal	Mesh	% Volatile matter	% Ash	% Moisture (air dry)	Swelling number
Wangaloa	85/150	50.5	2.15	Dried in N_2	0
Dauntless	85/120	49.9	2.12	6.83	1-2

Forms of Sulphur

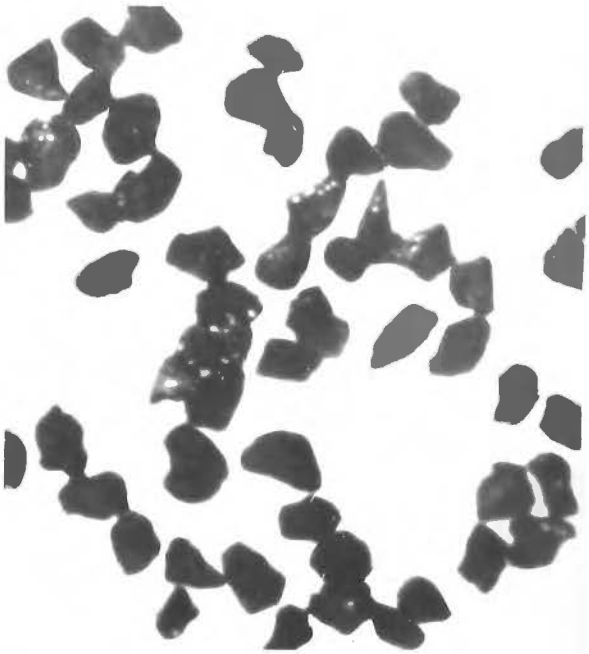
Coal	% Total sulphur	% Organic sulphur	% Pyritic sulphur	% Sulphate sulphur
Wangaloa	5.54	5.17	0.37	0.01
Dauntless	7.40	6.48	0.92	0.01

Replicate determinations were made of loss in weight for each run, a third being made and an average taken if the discrepancy exceeded 2-3%. No trouble occurred with Wangaloa coal, but initially some difficulty was experienced in obtaining agreement between replicate runs with Dauntless coal, at low temperatures. This was found to be due to a tendency

to stick to the sides of the tube; since this coal is only weakly caking, the main accumulations could easily be dislodged by tapping the tube at the end of a run. A new Incoloy DS tube had by this time (Run 343) been fabricated, to replace the old, badly corroded tube, and showed no tendency to produce scale, thus preventing significant contamination of the product. The runs with Dauntless coal did, however, show rather more scatter than those with Wangaloa, and the reason was, very probably, that some char was still retained within the tube and not measured. (N.B. This char would be burnt out before the succeeding run, since it was standard practice in all runs to allow air to pass up the tube for a few minutes after removal of the product.)

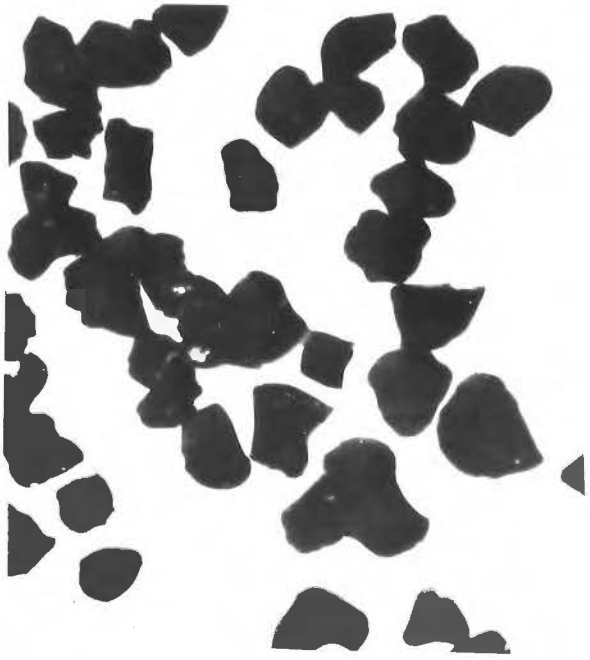
"Equilibrium" runs were carried out in exactly the same way as for Charming Creek coal. It is not certain, however, that the appreciably denser chars produced from these two coals (see Plate 7) were as efficiently agitated in the spouted bed that formed above the "constriction". Nevertheless, gas flow through the accumulation of char would certainly be sufficient to ensure rapid flushing away of volatile carbonisation products, and thus ensure that the decomposition could continue in a clean inert atmosphere. (N.B. The diameter of the hole at the base of the inverted conical constriction was 1/8", to give a higher velocity in the

COAL

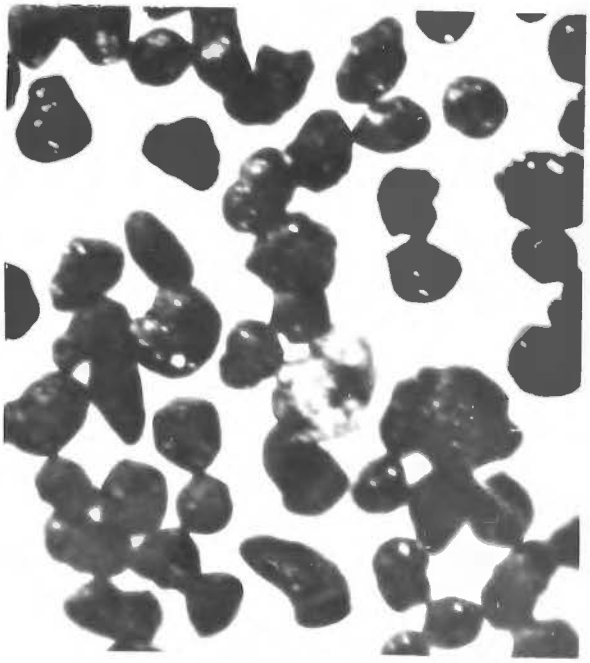


WANGALOA

CHAR 900°C



COAL



DAUNTLESS

CHAR 900°C

throat than in the experiments with Charming Creek coal.)

Due to the relatively small degree of conversion at 400°C, the data from these runs were more susceptible to errors in measurement of temperature and loss of weight than the runs at higher temperatures.

Hydrogenation of the chars was attempted in order to extend the results obtained in earlier experiments. However, the appreciably greater density of the particles meant that the bed of char showed a considerable tendency to fall through the constriction in the event of any mild fluctuation in pressure in the inlet gas line. This momentarily caused air to be sucked into the tube via the vent tube, and a series of minor explosions resulted. Since it was impossible to ensure that such pressure fluctuations did not occur, the experiments were rapidly abandoned.

As with the previous coals, samples were retained and analysed, of the residues from the volatile matter test.

Table 10

Properties of "Cokes" from Wangaloa and Dauntless Coals

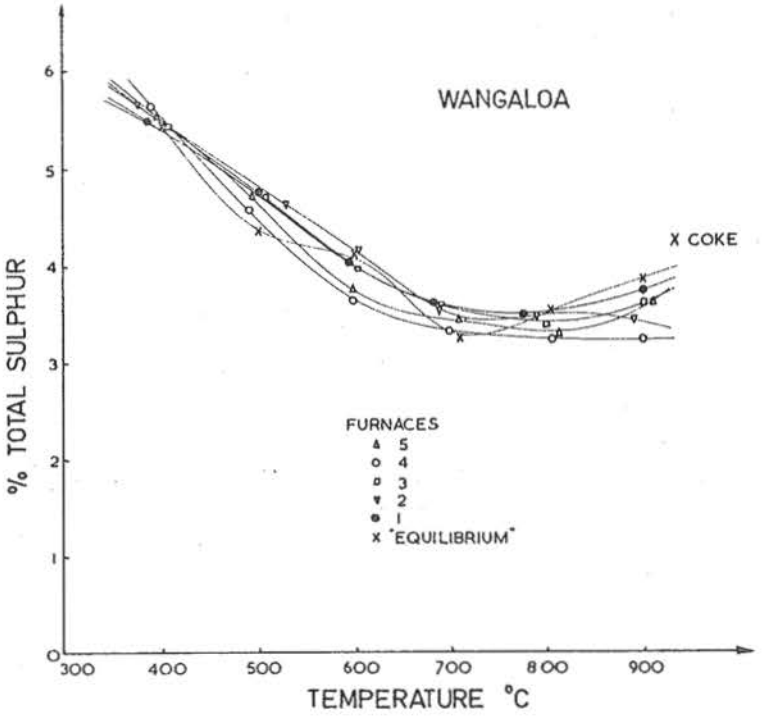
Coal	% Total sulphur	% Ash
Wangaloa	3.86	9.16
Dauntless	5.91	4.80

Results

Figs 25 and 26 show the variations of sulphur content and loss of weight, versus temperature, for each set of runs using one, two, three, four and five furnaces, and at "equilibrium". There is no real relationship between results using one particular arrangement of furnaces, but such a plot provides a useful means of graphical interpolation whereby results at a particular temperature may be estimated. This method was used in obtaining data at particular temperatures to enable decomposition versus time curves to be drawn.

From Figs 25 and 26 it is apparent that for both coals the extent of desulphurisation generally increases as the temperature approaches 800°C, but above this temperature there is a strong suggestion that this tendency is reversed.

Since the loss of weight during carbonisation had been directly measured in these experiments, the opportunity was taken (Figs 27 and 28) of comparing the loss of weight versus loss of sulphur relationships with those calculated according to the Volatile Matter and Ash basis methods (the latter for Wangaloa only, and not included in the diagrams). As was noted in the previous series of experiments, the correlation is most pronounced. Regression equations are



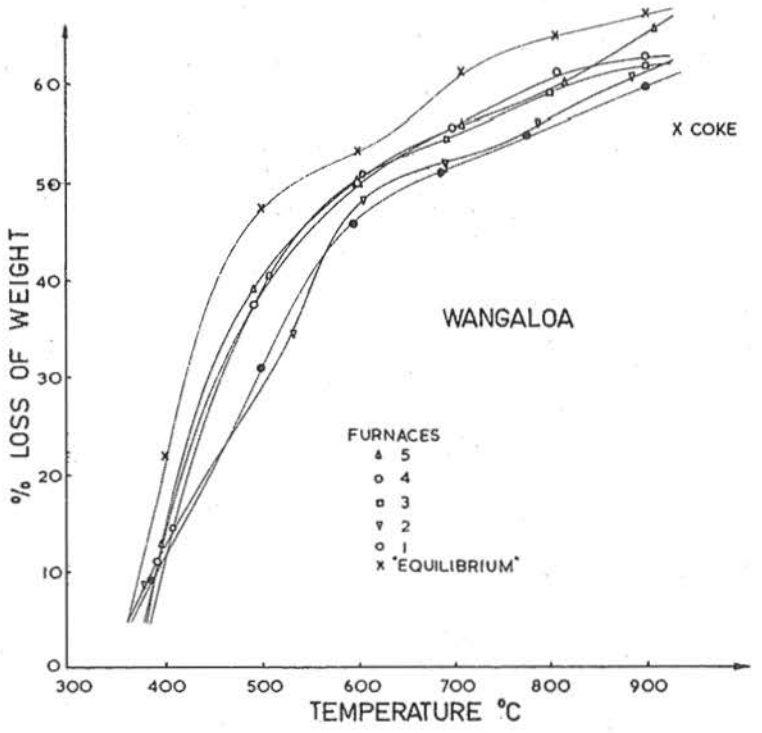
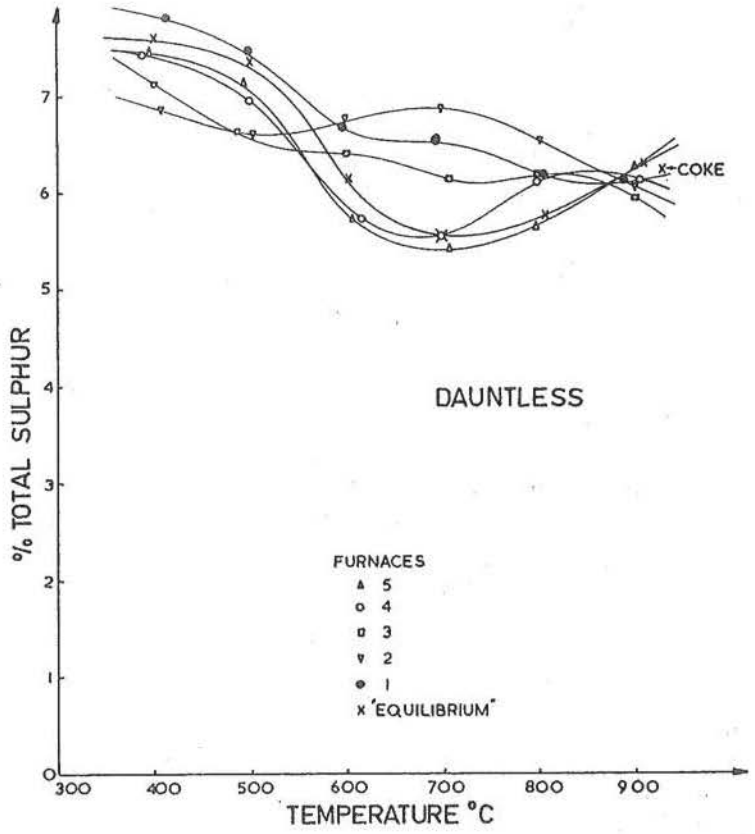


FIGURE 25 TOTAL SULPHUR AND LOSS OF WEIGHT CURVES - WANGALOA COAL.



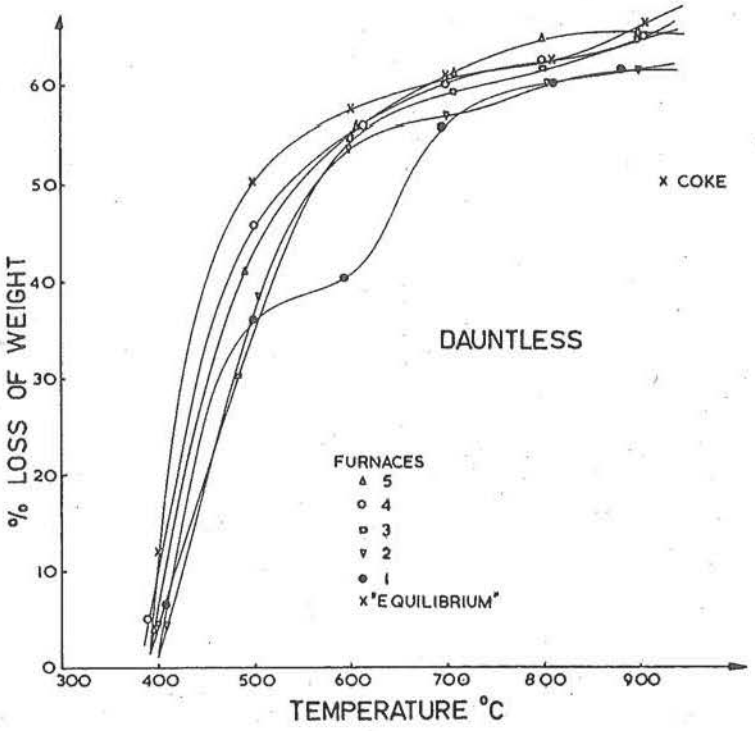
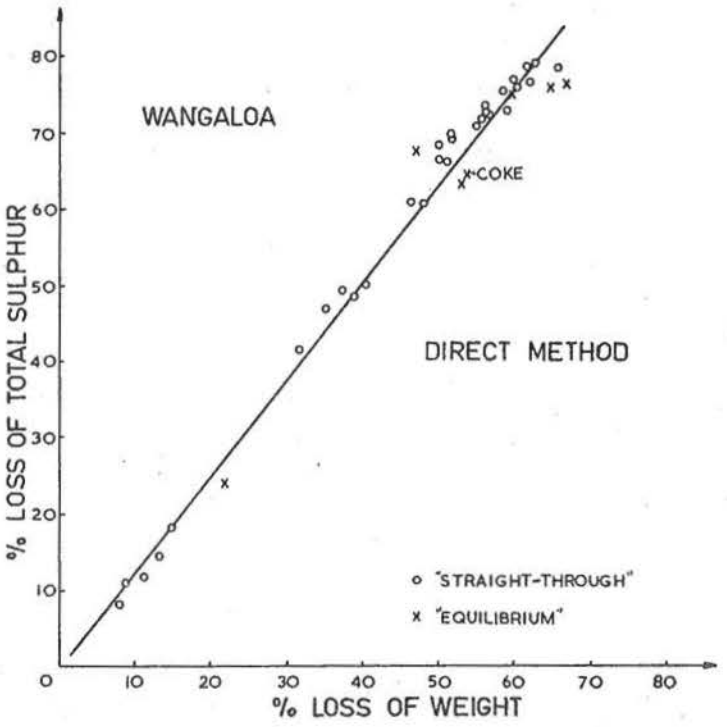


FIGURE 26 TOTAL SULPHUR AND LOSS OF WEIGHT CURVES - DAUNTLESS.



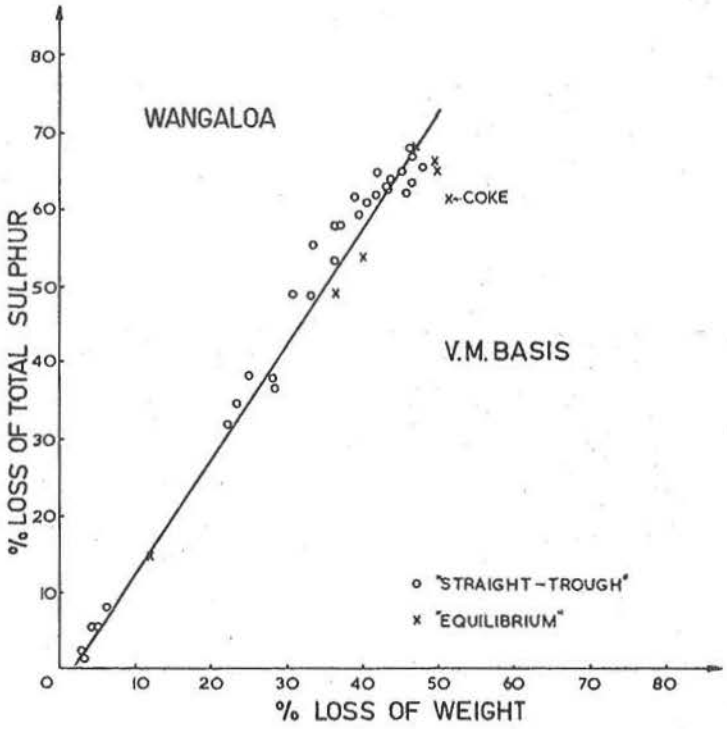
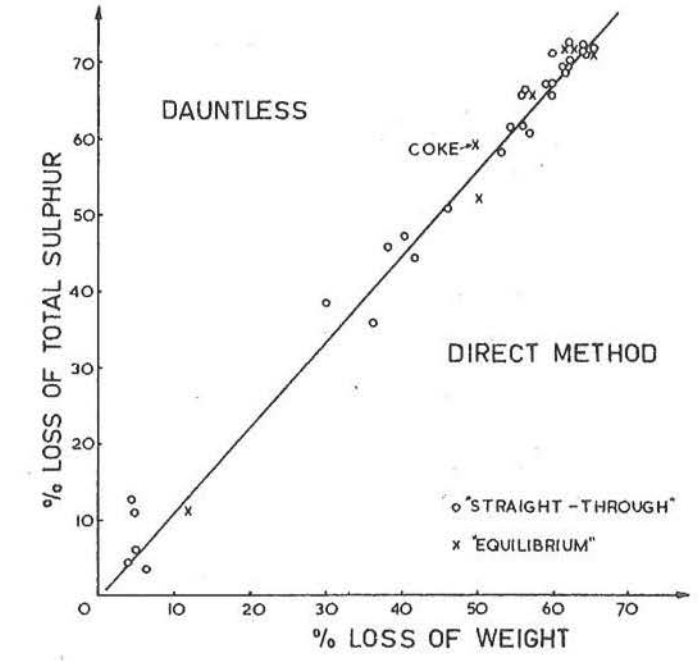


FIGURE 27 LOSSES OF WEIGHT AND TOTAL SULPHUR - WANGALOA.



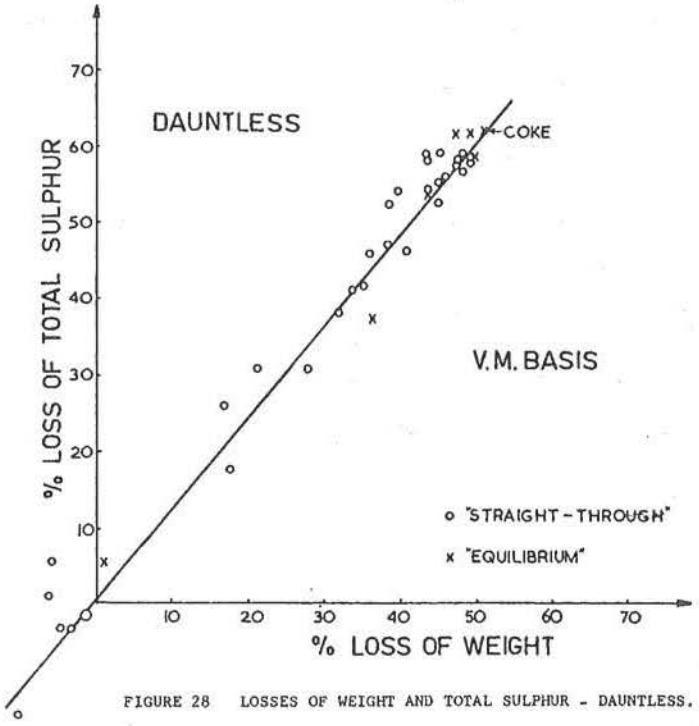


FIGURE 28 LOSSES OF WEIGHT AND TOTAL SULPHUR - DAUNTLESS.

Wangaloa $S = 1.27\ V + 0.005$ (Direct method)

$S = 1.46\ V + 5.09$ (Volatile matter basis)

$S = 1.315\ V - 19.24$ (Ash basis)

Dauntless $S = 1.09\ V + 1.62$ (Direct method)

$S = 1.15\ V + 3.60$ (Volatile matter basis)

(Correlation coefficients 0.99 in all cases, significant at $>$99.9% level.)

Negative values appearing in the Dauntless (V.M. basis) graph are almost certainly due to incomplete removal of moisture. (In correcting volatile contents to a dry, ash-free basis, it was assumed in all cases that the moisture had been entirely evaporated.)

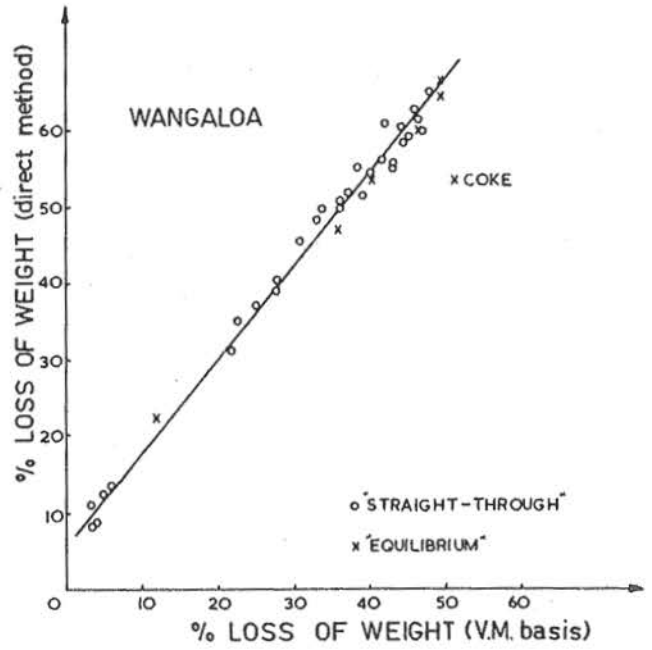
Fig. 29 shows the very close relationship that exists between losses of weight as measured, and as calculated according to the V.M. basis method. It is apparent that the V.M. content is an accurate means of estimating loss of weight, provided the proportionality factor has been evaluated. Regression equations were

Wangaloa $V_{VM} = 0.83\ V_{Direct} - 5.11$

Dauntless $V_{VM} = 0.91\ V_{Direct} - 10.74$

(Correlation coefficients 0.99 in both cases, significant at $>$99.9% level.)

In the preparation of graphs of decomposition against time, values were interpolated, as described earlier. Figs 30 and 31 show percentage losses of



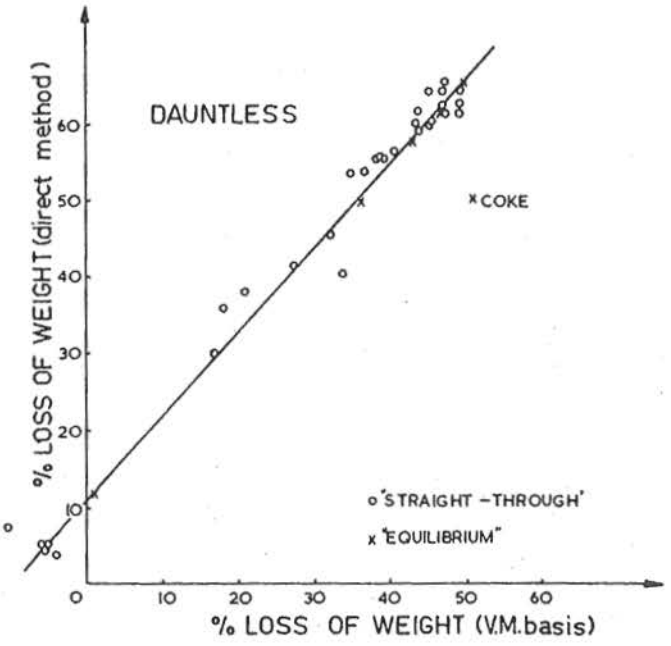
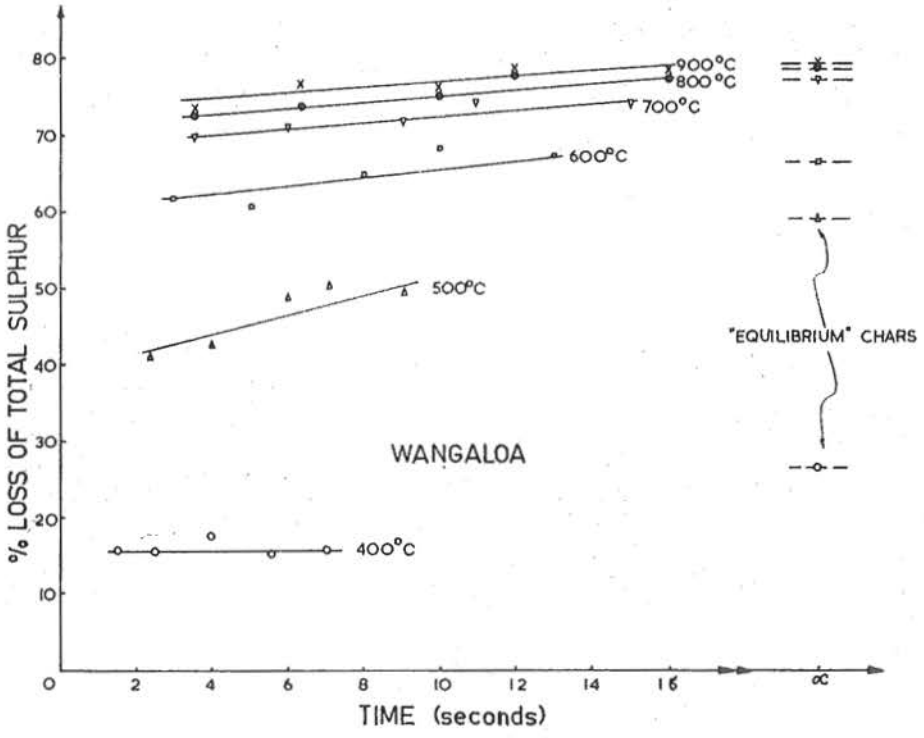


FIGURE 29 LOSSES OF WEIGHT, AS CALCULATED BY DIRECT AND V.M. BASIS METHODS, FOR BOTH COALS.

weight and total sulphur, as a function of time, at the six temperatures 400, 500, 600, 700, 800 and 900°C. Residence times were measured by visual observation for the fall through all five furnaces; for other arrangements, these times were proportionately reduced. The straight lines shown are not significantly different from the regression lines through the "straight-through" data.

It is apparent that by far the major part of decomposition occurs in less than two seconds; in the runs at higher temperatures, probably in very much less time. Since the data describe only the later stages of decomposition there is little to be gained in attempting to fit an arbitrary rate equation to the results. In any case, the scatter is probably too great for meaningful interpretation of what is, after all, only part of the overall process of devolatilisation.

The values of "equilibrium" loss in weight show that the extent of overall decomposition continues to increase, albeit slowly, with temperature, whereas the sulphur is virtually all volatilised by 700°C. This is almost certainly the explanation for the increase in sulphur content of the chars produced at the highest temperatures (Figs 25 and 26), since it is highly unlikely under the conditions of operation of the equipment that significant reabsorption of volatilised



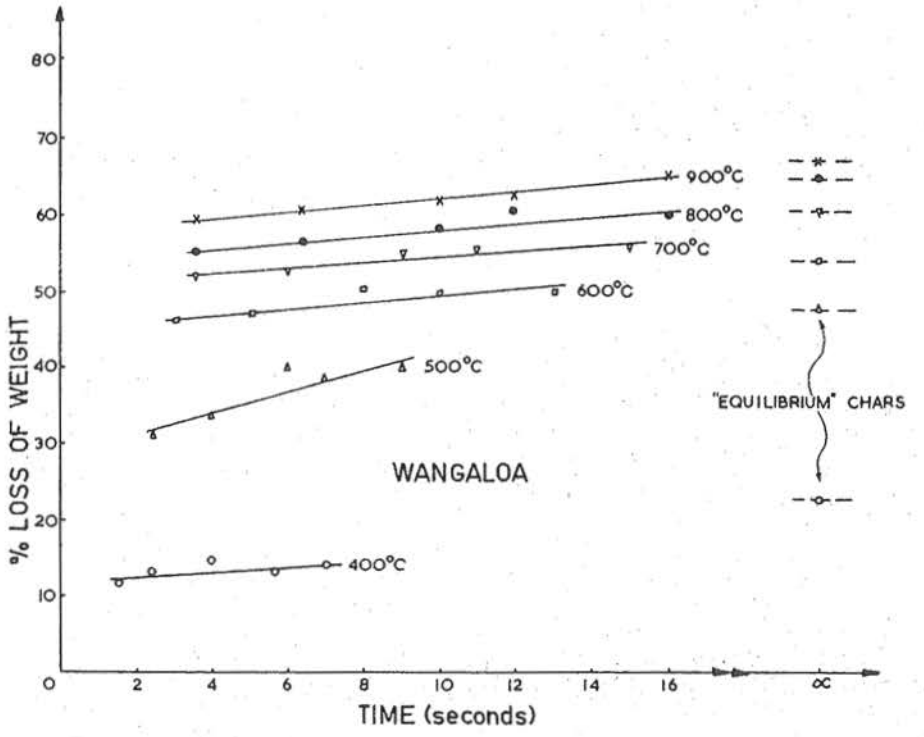
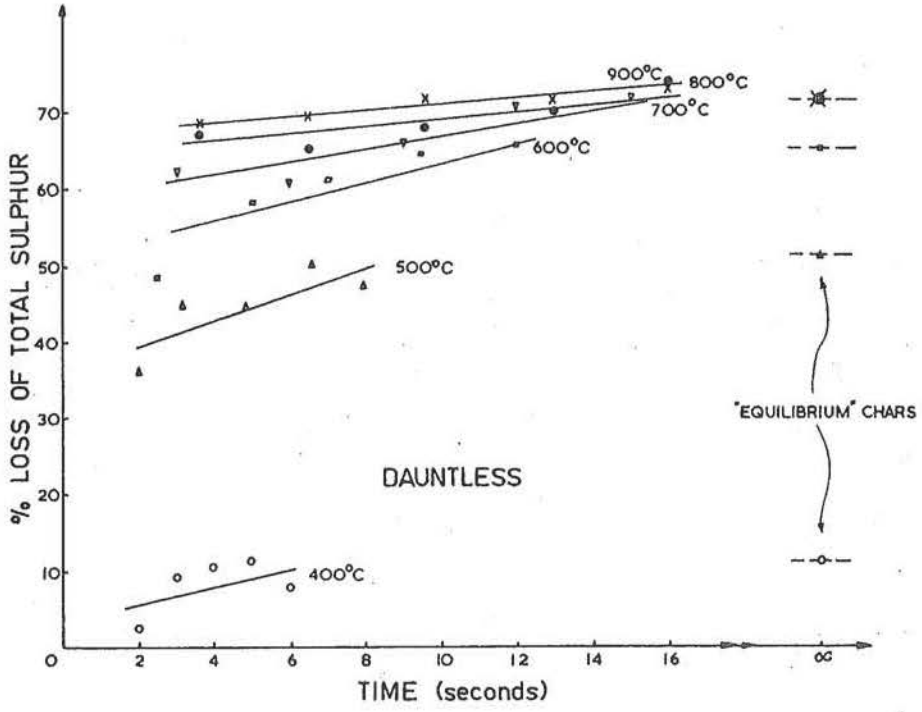


FIGURE 30 LOSSES OF WEIGHT AND TOTAL SULPHUR, AS A FUNCTION OF TIME, AT DIFFERENT TEMPERATURES - WANGALOA.



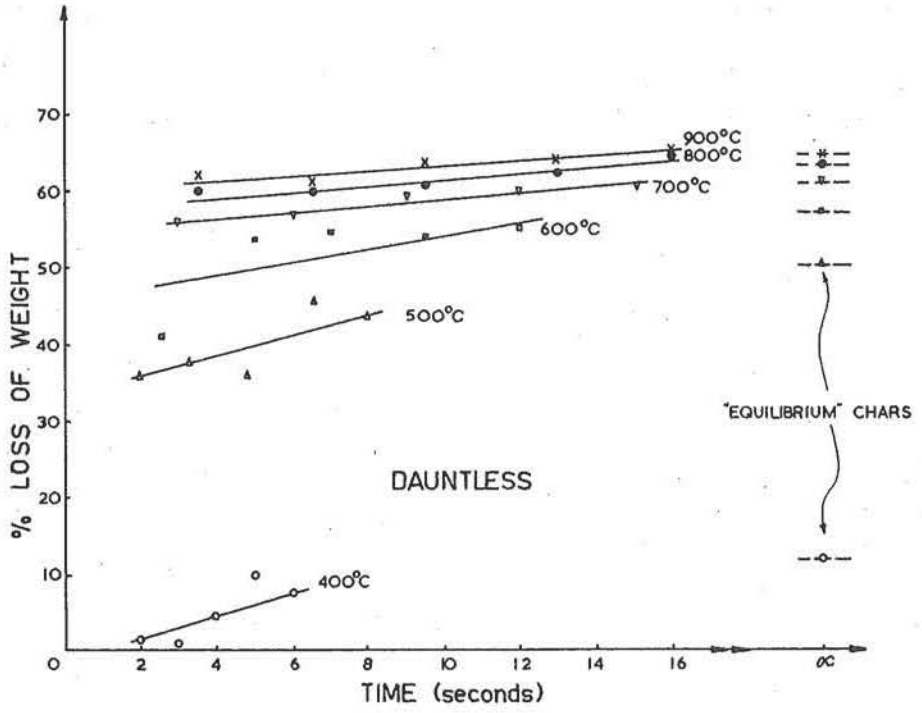


FIGURE 31 LOSSES OF WEIGHT AND TOTAL SULPHUR, AS A FUNCTION OF TIME, AT DIFFERENT TEMPERATURES - DAUNTLESS.

sulphur would have occurred. (It is possible that at the lowest temperature the char was not retained in the furnace long enough for "equilibrium" to be reached (average time for char was about 15-20 minutes in the apparatus). However, taking into account the high heat and mass transfer rates inherent in the use of small particles, the values measured are probably close to the "true" values.)

Interpretation of Data, in Terms of Reaction Kinetics

Simple First-order Reaction The simplest means of interpretation of the data, in terms of reaction kinetics, is to fit to a first-order rate equation, and evaluate the "activation energy". Since loss of weight and sulphur loss are so closely related, any general mechanism which describes the kinetics of loss of weight will presumably be adequate to describe sulphur loss, with adjustment of constants to take account of the proportionality factor.

(As explained in detail earlier, the reactions involved in carbonisation cannot strictly be treated by the methods of chemical kinetics; among other things there is the difficulty of defining the term "concentration". This latter problem can be evaded if a first-order reaction mechanism is taken as an

approximation, since concentration terms are eliminated and the specific reaction rate (i.e. rate constant) has the dimensions of $(\text{time})^{-1}$. There is no evidence, however, that coal decomposes according to a first-order mechanism, or indeed that the concept of order of reaction has any meaning at all in the solid state.)

The first problem that arises is that it is not possible to define an equilibrium state, against which extents of decomposition may be measured, in order to determine the conversion. Previous workers (Pitt, Chukhanov, etc) have assumed that the percentage of fixed carbon is independent of the method of carbonisation, but other workers (Yellow, etc) have since shown that this is not the case. The only other reasonable approach is to assume that all of the coal matter is potentially convertible to volatile matter, and express the fractional loss of weight as the conversion.

Let n_o be an initial quantity of coal, decomposing according to the first-order equation

$$\frac{dn}{dt} = - kn \quad \text{(where k = specific reaction rate)}$$

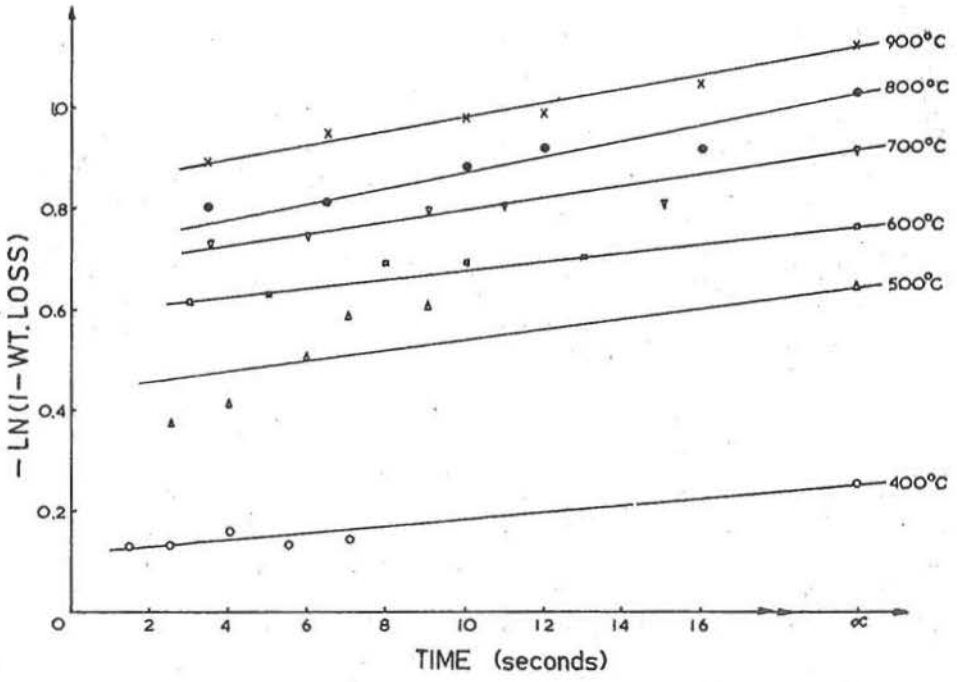
If this equation is integrated, from time t = 0 to t = t, we obtain

$$- \ln \left(\frac{n}{n_o}\right) = kt \quad \left(\text{where } \frac{n}{n_o} \text{ is (1 - fractional loss of weight)}\right)$$

Thus, if the reaction is adequately described by a first-order equation, a plot of (- ln n/n_o) versus t will be a straight line, of slope k.

To determine the activation energy, values of k obtained at different temperatures are fitted to the Arrhenius equation: $k = k_o \exp(-E/RT)$, by plotting (- ln k) versus 1/T. The straight line through the points is of slope -E/R, and the intercept on the ln k axis at $1/T = 0$ is k_o, the frequency factor.

This procedure was applied to the results for Wangaloa coal (Fig. 32). From the "straight-through" data, an average "activation energy" of 1.5 - 4.0 can be evaluated, but the correlation coefficients for the data at each temperature are not significantly different at the 95% level, so the only reliable conclusion that can be drawn is that the "activation energy" is approximately zero. With the "equilibrium" data included, corresponding to the lines drawn in Fig. 32, a similar result is obtained. The most likely explanation for this answer is that the assumption of an overall first-order reaction is an oversimplification, and that the "true" mechanism is much more complex. It is probable that this situation was encountered by Chukhanov (op cit) and accounts for his simplification of the overall decomposition reaction into three main stages; the above "straight-through" data would



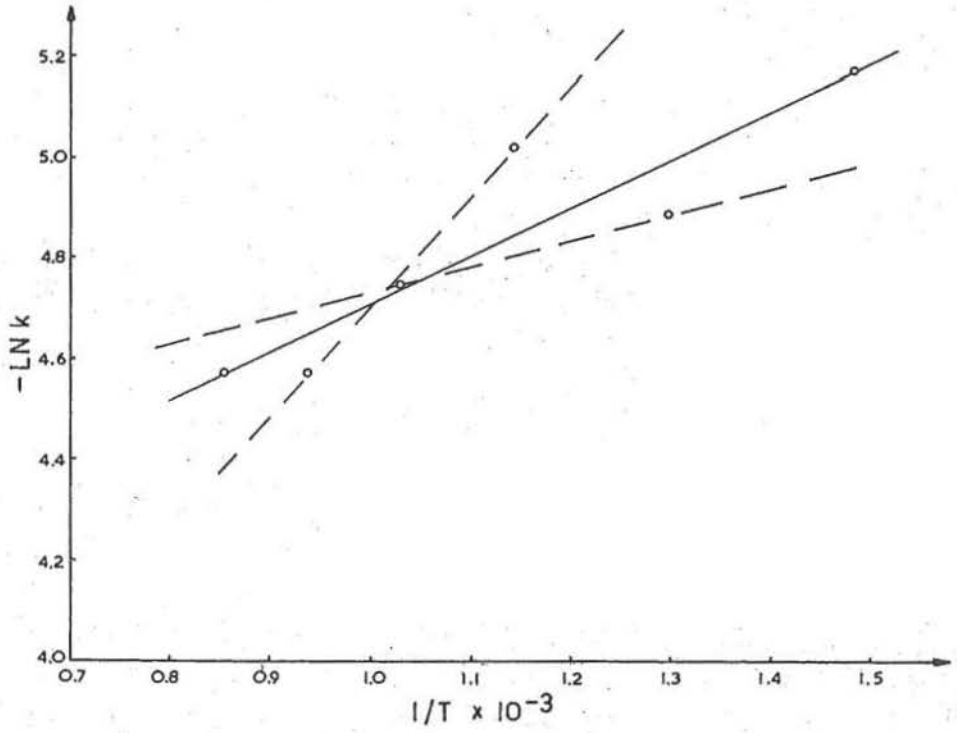


FIGURE 32 EVALUATION OF FIRST-ORDER REACTION RATE CONSTANTS AND "ACTIVATION ENERGY", FOR LOSS OF WEIGHT OF WANGALOA COAL.

approximately correspond to his second stage, and the "equilibrium" data to his third stage.

Pitt's Reaction Mechanism As described earlier, it is by now generally agreed that coal decomposes via a complex combination of series and parallel reactions; although undoubtedly correct, this theory is too general to be of any help.

The simplified theory of Pitt (op cit, p.50) is of greater assistance in this respect, since it postulates a specific reaction mechanism. The mathematical treatment of the theory may be summarised as follows:

Assume that all the decomposition reactions are first-order, that the frequency factors k_o are all equal, and that the number of molecules with activation energies between E and E + dE is proportional to f(E)dE.

Taking a large number (n_o) of molecules of various types but of equal molecular weight, these are allowed to decompose according to the first-order equations (1) and (2).

$$\frac{dn}{dt} = - kn \qquad (1)$$

$$k = k_o \exp(-E/RT) \qquad (2)$$

Of the $n_o f(E)dE$ molecules which initially have an activation energy E, after a time t the number remaining is

$n_o f(E) \exp(-k_o t \exp(-E/RT))dE$

The total number of molecules remaining is therefore

$$n_t = n_o \int_o^{\infty} f(E) \exp(-k_o t \exp(-E/RT))dE \qquad (3)$$

evaluated over the range of activation energies present.

An approximate method is required, in order to calculate f(E) from the values of $n_t/n_o \simeq$ (1 - weight loss). This makes use of the fact that the value of $F(E) \equiv \exp(-k_o t \exp(-E/RT))$ changes from being approximately 0 when E = 0 to being 1 when $E = \infty$; the change occurs rapidly at about the value $E_1 = RT \ln k_o t$ (4). It is therefore permissible* to replace F(E) by a step function which is zero for $E < E_1$, and unity for $E \geq E_1$. From equation (3) we have then

$$\frac{n_t}{n_o} = (1 - \text{wt loss}) = \int_{E_1}^{\infty} f(E)dE$$

From the experimental values of (1 - wt loss), the distribution curve f(E) may thus be reconstructed step by step, by evaluating E_1 at a number of different times

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*This approximation is not entirely reliable; by substitution of typical values of E_1 into the equation for F(E), it was found that at E_1, F(E) was equal to 0.39, and did not approach 0.95 until 4.4 Kcal above E_1. The error introduced by this approximation cannot therefore be ignored, although its effect upon the general shape of the distribution curve is probably small.

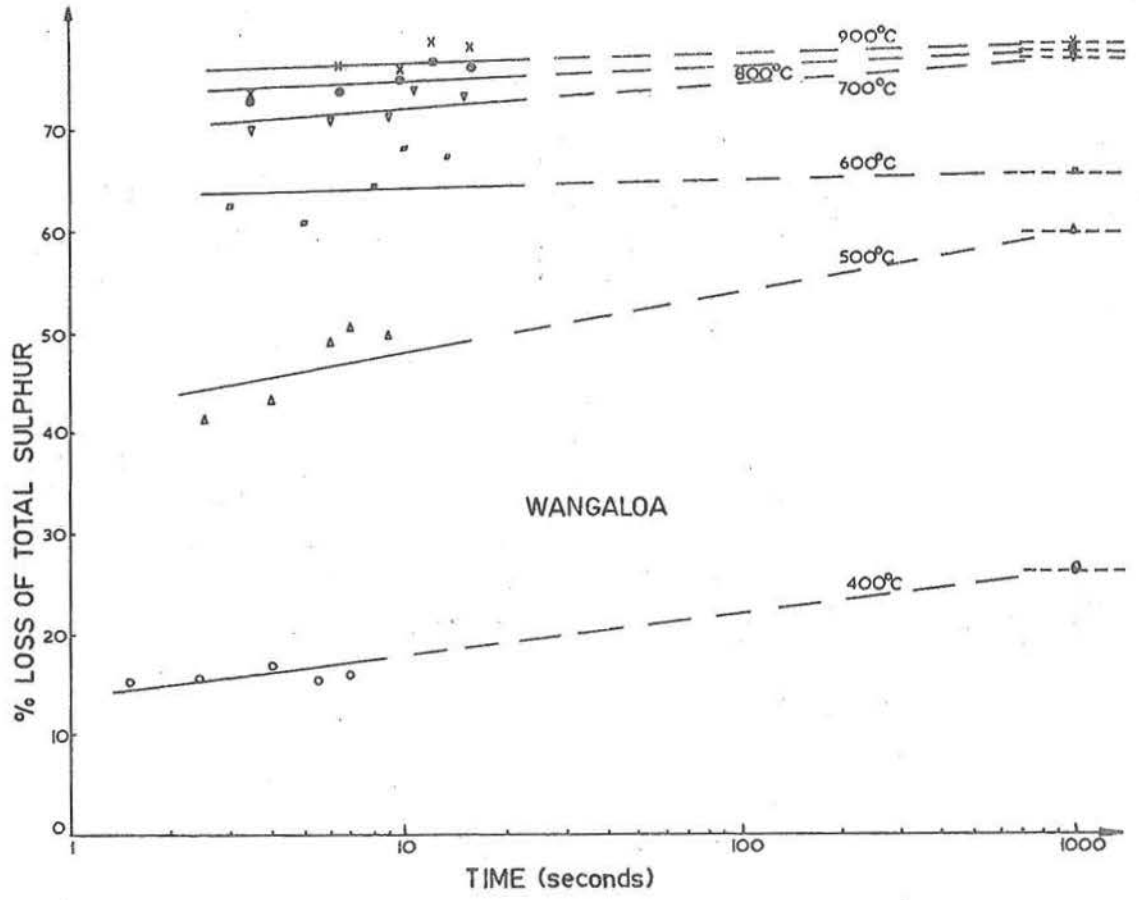
and temperatures from equation (4) and obtaining the area under the distribution curve from the corresponding values of (1 - wt loss).

Pitt's theory accounts for the change in "equilibrium" devolatilisation with carbonisation temperature,unlike the simple first-order mechanism already tried which assumes that devolatilisation proceeds to the same extent at all temperatures. However, application of the theory is complicated by the necessity to give a value to the frequency factors of the set of decomposition reactions. Pitt assumed that the reactions were of a chemical (i.e. bond rupture) nature, and took the value of 10^{15} minutes^{-1}; in the calculation described earlier, a value of about 1.1 - 1.3 minutes^{-1} was found, and the activation energy (1.5 - 4 kcal/mole compared with Pitt's value of 50 - 55 kcal/mole) was such as to indicate that the rate-controlling steps are of a physical, rather than chemical nature. (This conclusion is supported by that of Yellow (op cit) who states that, in disperse phase carbonisation, physical steps predominate; the reactions of high activation energy measured by van Krevelen[89] and others, and assumed by Pitt, are probably secondary processes such as cracking of high molecular weight products and tars.)

The large discrepancy between these sets of

values can almost certainly be attributed to a pronounced change in the controlling mechanism, and for this reason the use of Pitt's assumed value of k_o must be questioned, as far as the results of the work described in this report are concerned. An additional difficulty is that, due to the use of a logarithmic time scale, data are required over an extended range of times; in these experiments times were reasonably precisely known only from two to sixteen seconds, and such a range is too short to enable theoretical mechanisms to be fitted to any degree of significance. This is well illustrated by the graphs of weight loss and sulphur loss versus the logarithm of time for Wangaloa coal, Fig. 33. (The empirical relationship in which percent weight loss is a linear function of the logarithm of time was found by Pitt to be a close approximation to the devolatilisation curves predicted by his theory.) (The data corresponding to "equilibrium" have been arbitrarily associated with the decomposition time of 1000 seconds (17 minutes); this is reasonably close to the observed value, and in any case the slope of the line is relatively insensitive to variations of up to five or ten minutes in either direction.)

As will be seen, the data do not obey the linear relationship closely, a general upward trend being



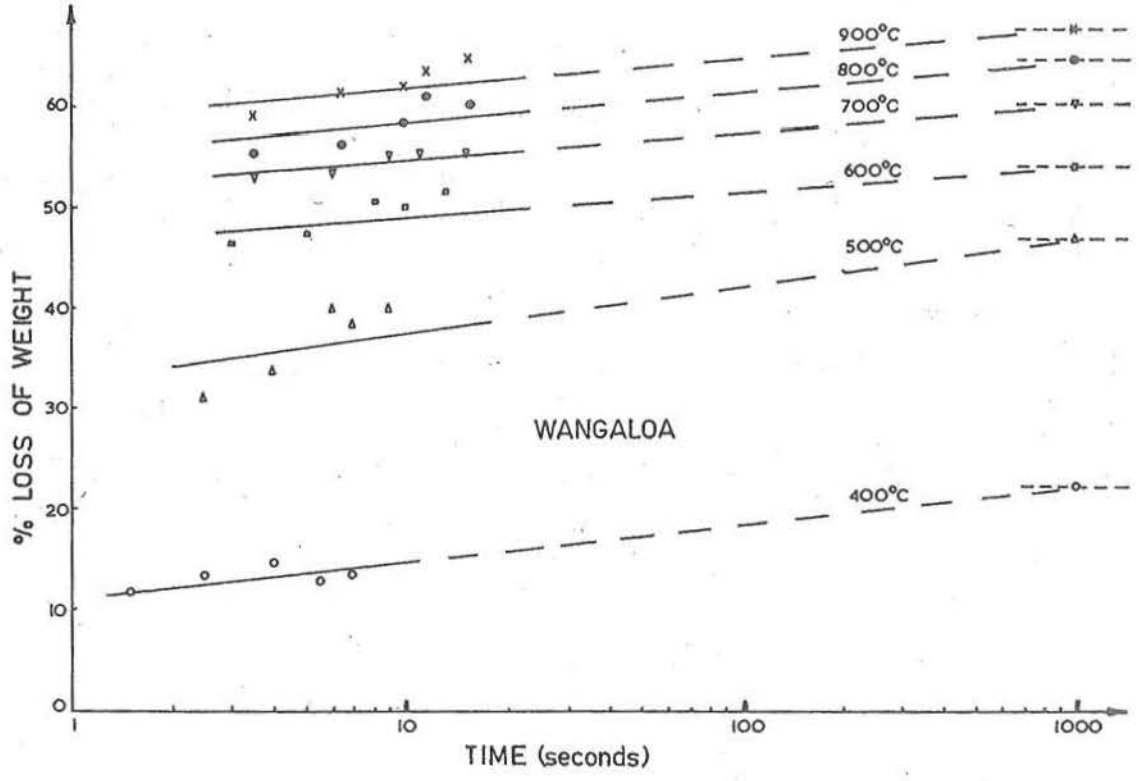
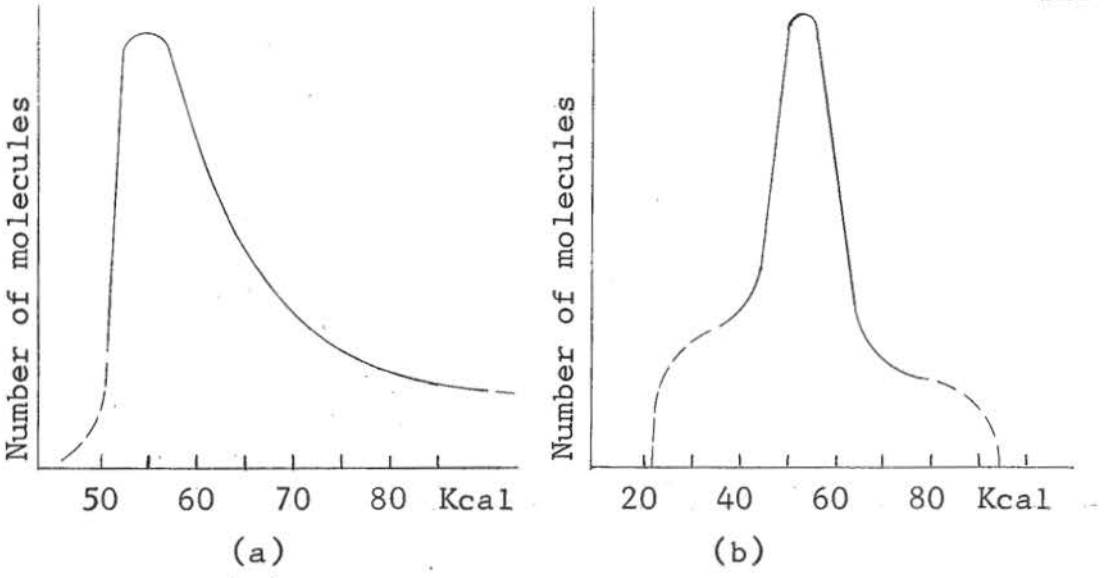


FIGURE 33 LOSSES OF WEIGHT AND TOTAL SULPHUR, AS A FUNCTION OF THE LOGARITHM OF TIME, FOR WANGALOA COAL.

observed at shorter times. The slope of the line drawn through the points, and the regression coefficient for the least well fitting set of data ($500^{o}C$, first five points only) were not significantly different when tested by the t-test, but the practical value of such a test is open to question when the number of degrees of freedom is so small.

Pitt's procedure was followed in estimating the distribution of "activation energies". The first value taken for k_o was 1.2 $minutes^{-1}$ (as determined earlier), from which initial calculations indicated that the majority of reactions contributing to the decomposition had negative activation energies. The next value tried was 10^{15} $minutes^{-1}$, as assumed by Pitt; these calculations gave results that were not significantly different from those of Pitt himself (50-55 kcal/mole). The distribution obtained was of the form shown below (a), compared with that of Pitt (b).

The long "tail" extending towards the higher activation energies results from the assumption that all of the coal matter is potentially capable of volatilisation.



Wangaloa coal Binley coal (Pitt)

It must therefore be concluded that, contrary to Pitt's assumption, the result appears to be predetermined by the value of k_o chosen for the calculations. The main reason for the difficulty in estimating k_o is, as already discussed, that the controlling steps in the devolatilisation reactions appear to be of a physical, rather than a chemical nature. The concept of an "activation energy" has no real theoretical significance in such a situation, and no assistance can be offered, by theory or by precedent, in determining a suitable value for k_o. While intuitively satisfying, Pitt's theory cannot be applied to the process of disperse phase carbonisation at the present stage of knowledge.

XIII. Analysis of Volatile Products

To obtain information as to the distribution of sulphur between the various carbonisation products, experiments were carried out to determine the amounts of sulphur in the gas and the tar, under conditions such that the coal was completely carbonised (i.e. with the constriction in place, as for the "equilibrium" runs).

Gas Analysis

The main experiments in this section involved the Department's Aerograph 90P-3 gas chromatograph, to analyse for hydrogen, carbon monoxide, methane, "unsaturateds", and hydrogen sulphide. Since hydrogen sulphide is irreversibly adsorbed on the silica gel column normally used[20] for separation of carbon dioxide in the analysis of permanent gases, the advice of the manufacturers was sought as to the best column packings and operating conditions. The system recommended[65] was 20 ft x 1/4 in. column of bis 2-2' (methoxy ethoxy) ethyl ether, 30% on 45/60 Chromosorb P (operated at 50°C) in series with a 20 ft x 1/4 in. 10% molecular sieve 5A and 90% molecular sieve 13X column, the latter mounted externally to the gas chromatograph, and

operated at room temperature. Thermal conductivity detection (detector cell temperature 80°C) was used, and a nominally 5 ml loop was fitted to the gas sampling valve. Carrier gas flowrates were in the region of 60 ml/min. for all runs.

The apparatus layout is shown in Fig. 34. The vacuum pump was required to assist the flow of gas through the sampling valve, because of the large pressure drop in this component. The first cottonwool filter removed particles of coke and some tar, and the second filter removed virtually all the remaining condensible and particulate matter.

Although nitrogen was the preferred carrier gas because of its presence in considerable excess in the gas from the furnace, carbon monoxide could not be measured accurately due to the closeness of their thermal conductivities.

For the runs with Charming Creek coal, argon (dry, welding grade) was used. To improve sensitivity for the runs with Wangaloa and Dauntlesscoals, each run was done twice; firstly with hydrogen (commercial), which enabled all gases but hydrogen itself to be detected, and secondly with nitrogen (dry, "oxygen-free") in order to measure the hydrogen content. Results from the two sets of runs were made compatible by taking the methane peak (easily and precisely

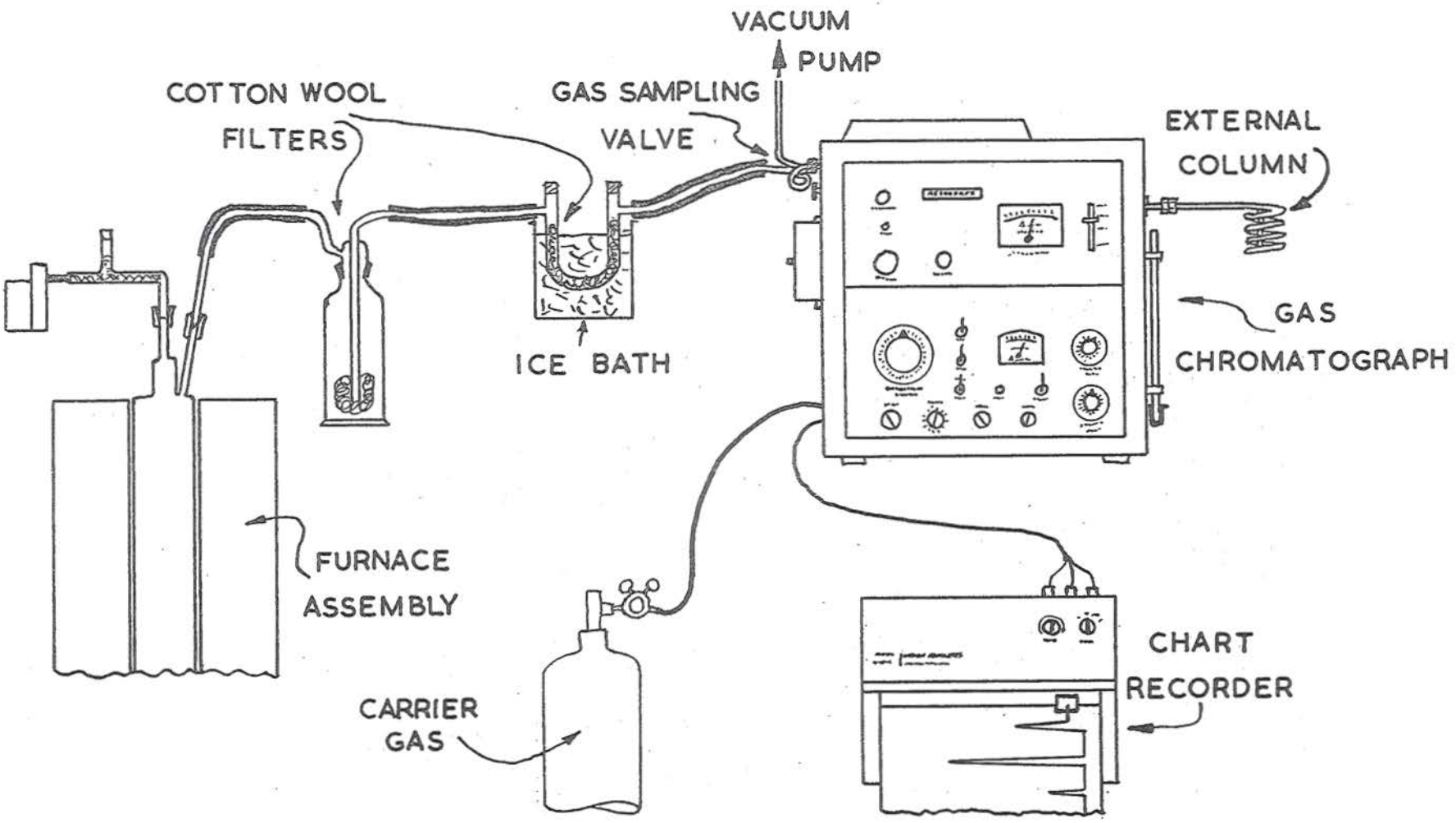


FIGURE 34 GAS ANALYSIS APPARATUS.

measurable in both cases) as a standard. The best carrier gas for the work would have been helium, but this gas was not readily available at a sufficient level of purity.

Table 11

Thermal Conductivities of Gases

Gas	Thermal conductivity λ/λ_{air} (0°C)	λ/λ_{air} (100°C)
Nitrogen	0.996	0.996
Hydrogen	7.15	7.10
Carbon dioxide	0.605	0.70
Helium	5.97	5.53
Methane	1.25	1.45
Ethane	0.75	0.97
Ethylene	0.72	0.98
Argon	0.68	0.71
Oxygen	1.01	1.03
Carbon monoxide	0.965	0.96
Hydrogen sulphide	0.51	not known

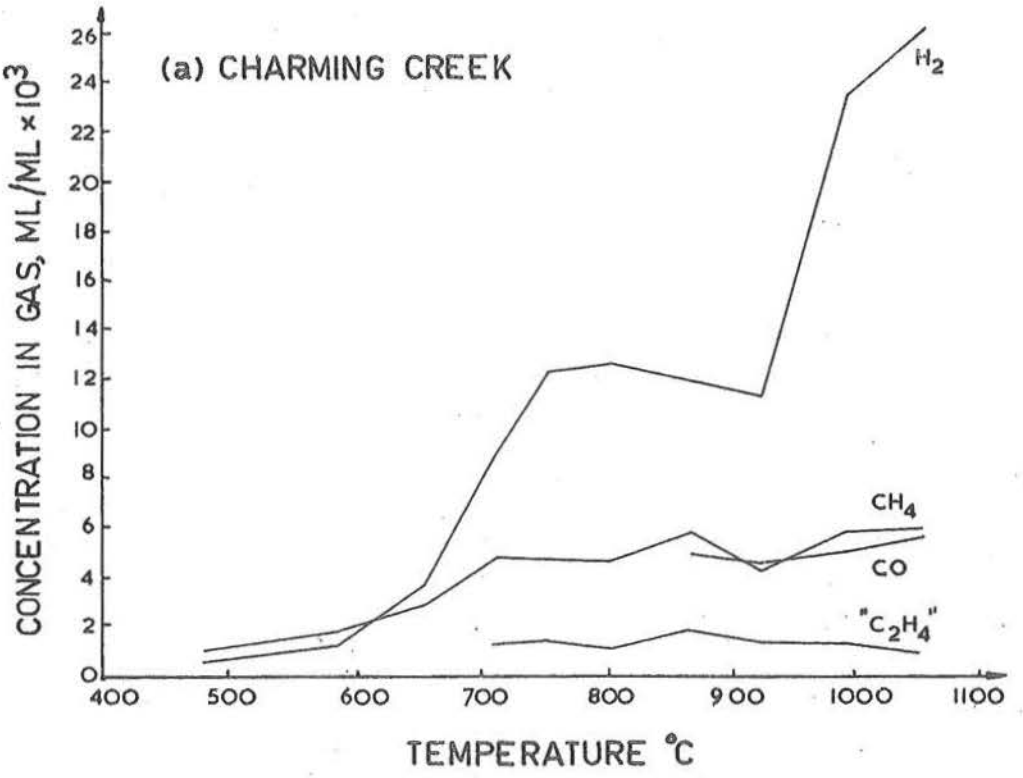
To obtain data from the recorder charts, it was assumed (vide Boreham[20]) that there was a linear relationship between peak height and volume of gas present. The instrument was calibrated with a sample of town's gas, using the analysis provided by the

Christchurch Gas Company. (The carbon dioxide, carbon monoxide and oxygen contents of the gas were checked with an Orsat apparatus; agreement was within 2-3%, which is quite adequate for this work.)

Results

Results of the analyses are shown graphically in Figs 25 and 26, together with the results of Groom[62], for Renown coal. The main point of interest is that no hydrogen sulphide was detected at any time. The threshold sensitivity of the instrument for this gas is not known, but since thermal conductivities differ appreciably it is not unreasonable to expect that, if present in significant quantities, it would have been detected.

To check this unexpected result, further experiments were carried out to determine whether hydrogen sulphide could be detected by other means. The method used was to pass the gas from the furnace directly into a solution of cadmium chloride or cadmium sulphate. According to Mason and Hakewill[101], both hydrogen sulphide and mercaptans (RSH) precipitate cadmium sulphide from cadmium chloride solution, but only hydrogen sulphide reacts with cadmium sulphate solution. Results of the experiments (furnace at 850°C, nitrogen



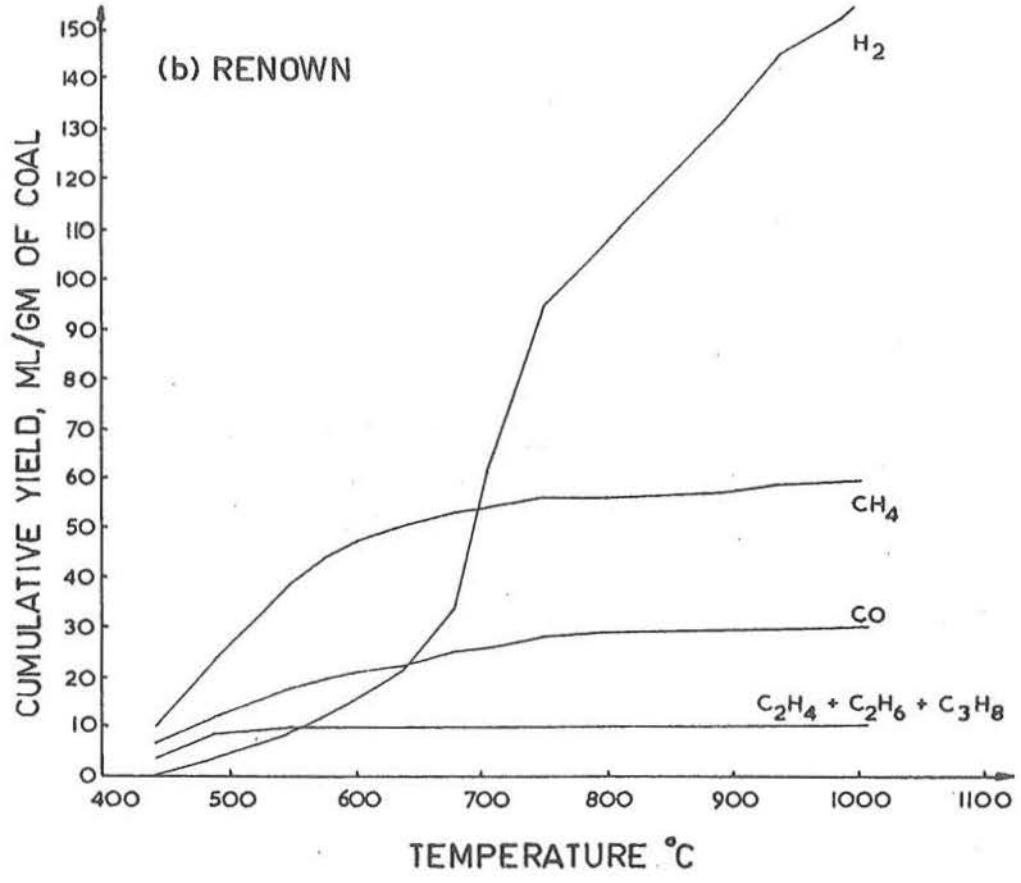
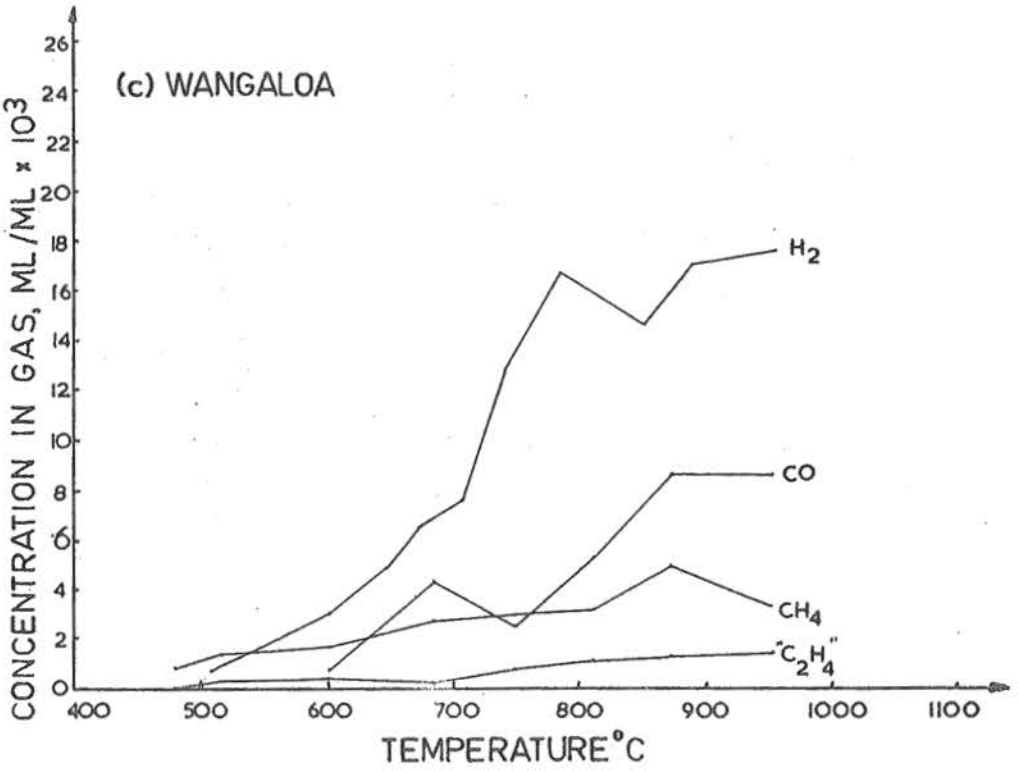


FIGURE 35 ANALYSIS OF GASES PRODUCED BY (a) DISPERSE PHASE CARBONISATION OF CHARMING CREEK COAL, AND (b) SLOW CARBONISATION OF RENOWN COAL (GROOM[62])



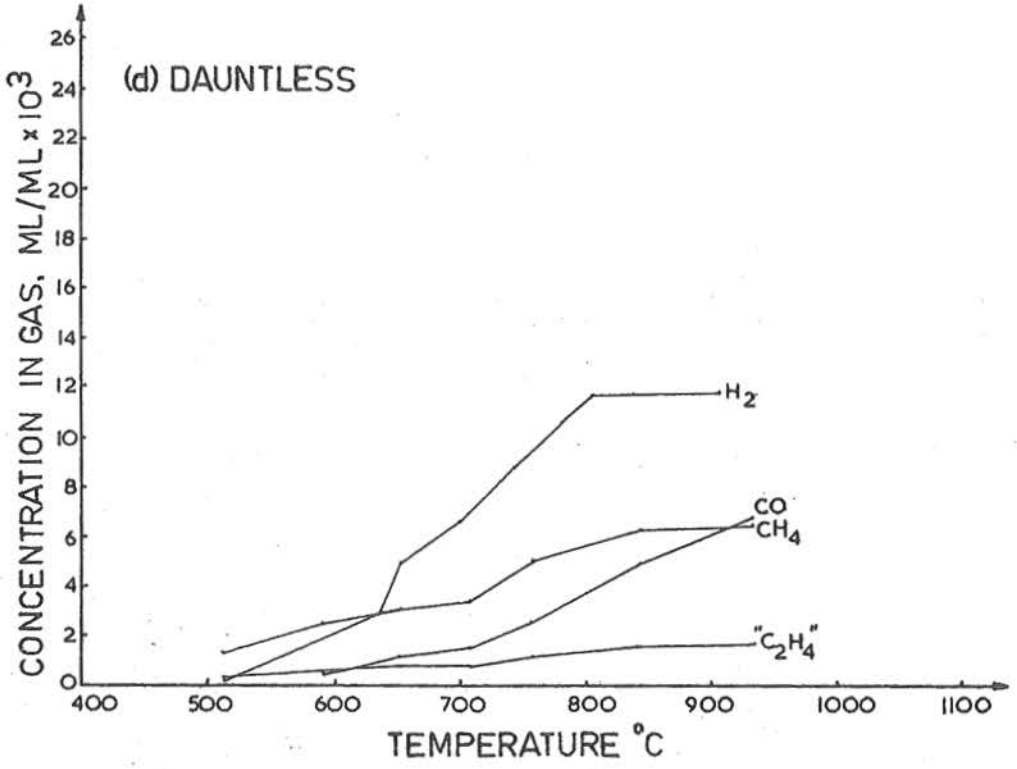


FIGURE 36 ANALYSIS OF GASES PRODUCED BY DISPERSE PHASE CARBONISATION OF (c) WANGALOA AND (d) DAUNTLESS COALS.

atmosphere) were as follows; cadmium sulphate did not react with Charming Creek gas, gave faint reaction with Wangaloa, and rather more with Dauntless (which may be attributable to the appreciably larger pyritic sulphur content of Dauntless coal). A large reaction was noted in all three cases with cadmium chloride solution.

The furnace was also run with a hydrogen atmosphere (Charming Creek only); a much greater reaction was noted with cadmium sulphate solution.

The main conclusion that can be drawn from these experiments, as far as high-speed coking in this type of equipment is concerned, is that hydrogen sulphide is not present in significant quantities as an initial product of the decomposition of organic sulphur in coal, but that a fair proportion of the volatilised sulphur is in the form of sulphides capable of reacting with cadmium chloride solution. In the presence of hydrogen, an appreciable proportion of the sulphur in the volatile matter and/or char is converted to hydrogen sulphide. It is probable that this hydrogen sulphide results mainly from hydrogenation of the char sulphur, but the possibility of vapour-phase reduction of high molecular weight volatile sulphur compounds cannot be discounted.

Other points of interest in the gas analysis

results are the abrupt decrease in the rate of hydrogen generation between 750 and 900°C with all coals. One possible reason for this decrease is that principal thermal decomposition is close to completion by 750°C (see Fig. 29). The increase in hydrogen generation above 950°C (noted with Charming Creek only - no experiments were done above this temperature with other coals, in order to avoid damage to the Incoloy tube) could be explained by vapour-phase cracking of volatilised hydrocarbons. Another interesting point is the steadily increasing concentrations of carbon monoxide with Wangaloa and Dauntless coals. It is not unlikely, however, that the presence of this gas may be due, in part, to combustion of char by small amounts of residual oxygen in the nitrogen supplied to the furnace. It is not certain that the curve marked "C_2H_4" is in fact due purely to unsaturated hydrocarbons; it is probable that saturated hydrocarbons such as C_2H_6 and C_3H_8 also contributed to this peak.

No results are available for the gas from slow carbonisation of Charming Creek coal; the only comparable work done on New Zealand coal is that of Groom[62], who analysed the gas produced from a modified Gray-King carbonisation assay apparatus, by gas chromatography. His results (for Renown coal, Waikato coalfield) are presented in Fig. 35, as the

cumulative yield of gas up to a given temperature. In this form, they are qualitatively comparable with the results for rapid coking. Because of the difficulties of measuring nitrogen and coal rates precisely, the errors involved in estimating the volume of gas generated from the coal were greater than the volume itself; for this reason, the conversion of gas concentrations to yields per unit weight of coal was not practicable. The extent of agreement between the two sets of data is better than expected, taking into account the differences inherent in the two coking processes, and the differences in the characteristics of the two coals. (Groom also gives the proportions of oxygen, nitrogen, and carbon dioxide in the gas. His separate results for ethane, ethylene and propane have been summed.)

Tar Analysis

It can be inferred from the results quoted above that a proportion of the volatilised organic sulphur is in the form of high molecular weight compounds, which would probably be condensible as tar.

To test this hypothesis, an air condenser (a six-inch length of half-inch bore glass tubing) was fitted to the gas outlet from the furnace, and left

for some hours to enable a film of tar to build up. The temperature of the condenser was about 50-100°C, which would enable a fairly uniform sample of the tar to be trapped. The tar film was dissolved in a small quantity of pure methyl cyclohexanone and the extract placed in a crucible. The solvent was removed by evaporation over a water bath, and drying in an oven at 105°C. The total sulphur content was found by covering the residue with Eschka mixture, igniting, and determining in the usual manner.

Results for the tars collected at 850°C were Charming Creek - 3.8%, Wangaloa - 4.3%, and Dauntless 3.65% total sulphur, which confirms that the tars are rich in organic sulphur.

XIV. Summary and Conclusions

Three types of high-organic-sulphur coal have been carbonised rapidly, in such a way as to minimise contact between the volatile products and solid residue. The percentage loss of sulphur (S) was found to be directly proportional to the overall loss of weight (V), according to the general relation

$$S = aV + b$$

In the coals studied in this project, the constant "a" was always greater than unity (which agrees with the claim of Angelova and Syskov[3]) indicating that organic sulphur is present in a rather less thermally stable form than the rest of the coal matter. The constant "b" is probably closely related to the evaporation of absorbed or adsorbed water during the initial stage of carbonisation.

The only comparable results located by the writer, on the fixed-bed carbonisation of high-organic-sulphur coals over a range of different temperatures, are those of Goswami and Roy, and Marshall and Draycott (op cit Table 3). From their data, it is possible to calculate loss of sulphur versus loss of weight, as shown in Fig. 37. It will be seen that their results have little in common with those obtained in the present work. It seems highly probable that, in

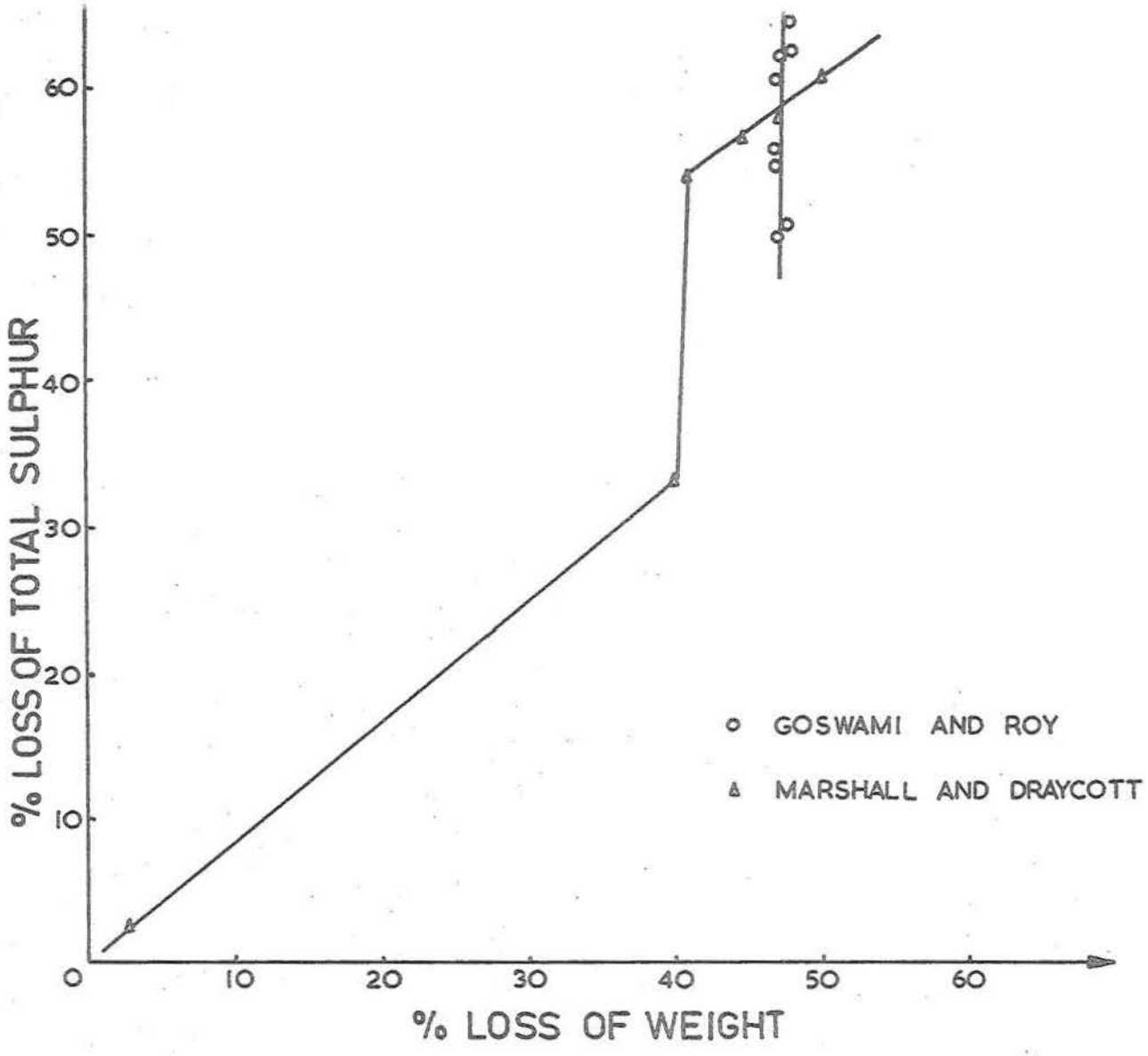


FIGURE 37 LOSSES OF WEIGHT AND TOTAL SULPHUR, FOR THE SLOW CARBONISATION OF BARAGOLAI COAL (GOSWAMI AND ROY[61]), AND TANGORIN COAL (MARSHALL AND DRAYCOTT[100])

a fixed bed of carbonising coal, emission of sulphur is complicated by cracking of high molecular weight volatile products, and reaction of volatile sulphur compounds with the hot coke.

Hydrogenation has been shown to be effective in removing sulphur from char; this process is noticeable above 550°C, but does not become significant until about 700°C. Results confirm the conclusions of Zielke et al (op cit Table 3(a)), that the initial loss of sulphur is rapid, and that it soon decreases and approaches the overall rate of gasification of carbon. Hydrogenation for short periods is therefore an effective means whereby the sulphur content of char may be significantly reduced with no great decrease in yield.

Attempts have been made to interpret the decomposition data, in terms of reaction kinetics; a simple first-order mechanism gave a near-zero "activation energy", and use of the reaction mechanism described by Pitt (op cit) was complicated by the necessity to assume a frequency factor. The main conclusion that can be drawn is that the rate-limiting steps in disperse phase carbonisation are of a physical, rather than chemical nature, and cannot legitimately be described in terms of conventional chemical kinetics. This conclusion is in agreement with those

of other workers.

The high yields of tarry condensibles indicate support for Yellow's theory (op cit) that the primary products of carbonisation are high molecular weight fragments, which subsequently decompose in the vapour phase. It appears that very little of the sulphur is volatilised as hydrogen sulphide, a large proportion being in the form of mercaptans.

No obvious correlation is apparent between the types of coal used and the differences in their experimental behaviour. Explanation of these differences (particularly as concerns the constant "a") may not be possible until it is known what types of sulphur compound are present in the coals, and in what proportions.

This project originated in a desire to investigate the possibility of production of low-sulphur coke from high-sulphur coal. It has been shown that disperse-phase carbonisation gives char of an appreciably lower sulphur content than that obtained from fixed-bed carbonisation, but only at the cost of a much lower yield; this process may well be of greater potential as a means of gas production, by virtue of the correspondingly high yield of volatile products. The suitability of the char for metallurgical purposes is

somewhat doubtful, although briquetting might assist its utilisation in this respect.

Further Work

The writer considers that the subject is worthy of further study, and suggests that work be maintained along two main fronts.

Firstly, investigation into the basic chemistry of sulphur in coal, in an attempt to obtain more information as to the types of organic sulphur groupings present in the coal "molecule". Solvent extraction and fractionation, combined with the use of infrared and mass spectroscopy to identify the products, would probably be the most promising technique.

Secondly, continuation of the present work on rapid carbonisation, with greater emphasis being given to the analysis of volatile products, particularly the tarry condensibles. Vacuum carbonisation shows promise in this respect, in that it permits short residence times and minimum degradation of volatilised organic matter.

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Appendix 1

Derivation of equations for Volatiles Losses, according to Volatile Matter and Ash Basis methods.

V.M. Basis

In the B.S. test method (on a d.a.f. basis),

100 gm coal = V_{coal} gm volatiles + (100 - V_{coal}) gm coke.

In the general case, V% volatiles are lost by the coal during coking, i.e.

100 gm coal = V gm volatiles + (100 - V) gm char.

Now, assuming that the maximum volatile evolution (as measured by the B.S. method) is the same, no matter how the coking is done,

$$(100 - V) \text{ gm char} = (100 - V_{coal}) \text{ gm coke} + \frac{V_{char}}{100} \times (100 - V) \text{ gm volatiles}$$

$$\therefore (100 - V)\left(1 - \frac{V_{char}}{100}\right) = (100 - V_{coal})$$

$$\therefore V = 100 - 100\,\frac{(100 - V_{coal})}{(100 - V_{char})}\ \%$$

It is also possible to calculate the proportion of original volatile matter remaining in the coal, P (vide Pitt[75]).

From above,

$$P = \frac{\frac{V_{char}}{100}(100 - V)}{V_{coal}}$$

Substituting for V,

$$P = \frac{V_{char}}{V_{coal}} \times \frac{100 - V_{coal}}{100 - V_{char}}$$

Ash Basis

100 gm coal = A_{coal} gm ash

100 gm char = A_{char} gm ash

$\therefore$ $\frac{A_{coal}}{A_{char}}$ gm char = A_{coal} gm ash

$\therefore$ Volatiles loss = $100 - \frac{A_{coal}}{A_{char}} \times 100$,

on total coal basis.

On ash-free basis,

$$\text{Volatiles loss} = 100 - \left(\frac{A_{coal}}{A_{char}} \times 100 - A_{coal}\right)$$

$$= 100 - \frac{A_{coal}}{A_{char}} (100 - A_{char}) \%$$

Sulphur Loss

V.M. Basis

Per 100 gm coal, S in coal = S gm in char + S gm lost in volatiles.

$$\therefore S\% \text{ lost} = S_{coal} - S_{char} \times \frac{(100 - V_{coal})}{(100 - V_{char})}$$

$$\therefore \% \text{ loss of original coal sulphur} = \frac{S_{coal} - S_{char} \times \frac{(100 - V_{coal})}{(100 - V_{char})}}{S_{coal}} \times 100$$

Ash Basis

By a similar method,

$$\% \text{ loss of S} = \frac{S_{coal} - S_{char} \times \frac{A_{coal}}{A_{char}} \left(1 - \frac{A_{char}}{100}\right)}{S_{coal}} \times 100$$

Experimental Runs - Series I

Run	Temperature	Coal	% Sulphur	Remarks
1	850	Stockton	-	Trial injection
2	"	"	-	Trials, with H_2 and N_2
3	"	"	-	Blockage in injector
4	"	"	-	Mixture carborundum/coal. Blockage.
5	"	"	-	As above, increased gas flow. "
6	"	"	-	" " , blockage.
7	"	Stockton 60/72	-	Blockage.
8	"	" "	-	"
9	"	" 44/52	-	Most of coal in before blockage.
10	"	" 22/30	-	Blockage, due partly to large particles.
11	"	" 44/52	-	High gas flows - minor blockage.
12	"	" 60/72	-	Early blockage.
13	"	" 85/100	-	Rapid injection - early blockage.
14	"	" 44/52	-	Empty bed. No reaction in absorber.
15	"	" 60/72	-	Empty bed. No reaction in absorber.
16	"	" 44/52	-	Shallow bed. Blockage.
17	"	" 60/72	-	Rapid injection. Blockage.
18	"	" 85/100	-	Partial blockage. New bed material.
19	"	" 85/100	-	Slight blockage. Added more carborundum.
20	"	" 85/100	-	Agglomeration in bed. " " "
21	"	" 100/120	-	Blockage. Cleaned silica tube.
22	"	" 72/85	-	Empty bed. No reaction. Lot of smoke.
23	"	" 72/85	-	" " As above.
24	"	" 72/85	-	" " " "
25	750	Dauntless 60/85	-	Injection O.K. Bed agglomerated.
26	"	Stockton 44/52	-	Blockage.
27	"	Dauntless 60/85	-	Injection O.K. Large reaction.
28)				
29)	Calibration runs, at different temperatures.			
30)				
31	770	Various	-	Top off bed. Observed behaviour.
32	745	Stockton 44/52	4.0	Too much S.
33)				
34)	Calibration runs.			
35	-	Stockton 44/52	-	Blockage in absorber.
36	-	"	-	Run abandoned - injector broke.
37	-	"	-	Blockage in inlet - low gas rate.
38	-	"	-	" " " " " "
39	-	"	-	Top off bed. Nc agglom. if injection very slow.
40	625	"	0.72	Slight blockage and agglomeration.
41	-	-	-	Sample lost.
42	610	"	1.0	Blockage.
43	615	"	0.13	Using N_2 - blockage.
44	640	"	0.87	Agglomeration.
45	640	"	1.0	Slight agglomeration.
46	640	"	1.2	Blockage near end. High flows and slow injection.
47	640	"	0.3	Different analysis method.
48	680	"	0.9	As 47 - slight blockage.
49	Trial run, with top off and empty bed, to observe behaviour.			
50	705	"	0.1	Top off, empty bed. No reaction.
51	Calibration run, with coarser bed material. Trial injections.			
52	Silica packed tube removed, and absorber connected directly to outlet from bed. Trial injections.			
53	700	"	-	Top off, trial injections. Agglom.
54	Trial injections, top on and new absorber system.			
55	660	"	(0.8)	Error in analysis.
56	730	"	-	Discovered separate I_2 titrations.
57	-	"	-	Attempt to detect SO_2. Abandoned.
58	600	"	-	As 57 - negligible reaction.
59	750	"	0.8	Analysis for both H_2S and SO_2. $NaSO_2$
60	700	Dauntless 44/52	1.65	Lot of dirt and soot in absorber.
61	750	"	-	Separate I_2 titrations.
62	750	"	1.2	As 61. Initial titre 0.3% S.
63	690	"	1.59	Reverted to original analysis method.
64	700	"	1.82	As 63.
65	700	"	-	Comparison of I_2 titration results.
66	710	"	0.15	Using acidified cadmium chloride.
68	710	"	2.52	Small amount of coal, very slowly injected.
67	Run abandoned - breakage of injector.			
69	Calibration run.			
70	720	Dauntless 44/52	3.32	As 68.
71	740	"	2.9	As 68.
72	770	"	3.38	As 68.
73	700(?)	"	3.14	As 68.
74	Calibration run.			
75	780	"	2.66	Dirty deposits in absorber. No tar.
76	780	"	2.53	Slightly more tar.

Run	Temperature	Coal	% Sulphur	Remarks
77	750	Dauntless 44/52	(1.25)	Errors in analysis.
78	730	"	1.80	Lot of solid matter. Fresh solutions.
79	750	"	2.78	New solutions - better.
80	750	"	3.9	Generation of H_2S slower than rest of volatiles.
81	750	"	1.43	Some fine ppt in absorber after titration.
82	750	"	4.73	Very slow injection.
83	750	"	3.96	" " "
	Replaced silica furnace.			
84	740	"	6.78	Solution in absorber much cleaner.
85	770	"	3.11	Separate I_2 titrations.
86	770	"	3.12	Slight tar formation.
87	770	"	4.72	About 2 mins on H_2, before and after injection.
88	710	"	2.05	5 mins before and after.
89	730	"	2.51	Slight blockage.
90	710	"	5.45	15 mins on H_2 before and after.
91	640	"	3.42	2 hrs " " " "
92	710	"	2.55	As above, no H_2S noted after 10 mins.
93	670	"	2.55	Some soot and tar.
94	670	"	1.55	As 93.
95	830	"	6.15	3 hrs on H_2 after. Still H_2S after 3 hrs.
	Use of water injection.			
96	-	-	-	Water dropper broke - modified.
97	680	"	1.84	Tarry deposits.
98	680	"	3.85	3 mins on H_2 after. Very little tar.
99	680	"	4.79	Silica furnace hotter.
100	680	"	4.79	As 99, 10 mins on H_2 after.
101	680	"	4.61	As 100, 5 mins on H_2 after.
102	680	"	5.36	As 101, 10 mins on H_2 after.
103	850	"	3.62	Higher temperatures.
104	870	"	3.56	As 103.
105	850	"	4.07	As 104, higher water rate.
106	790	"	1.92	Packing installed in water inj. tube.
107	-	-	-	Run abandoned - weighing error.
108	800	"	6.8	As 106. Excessive S detected.
109	735	"	4.1	As 108.
110	-	-	-	Run abandoned - analytical error.
111	740	"	4.63	Poor end-point.
112	735	"	4.29	As 111.
113	735	"	3.14	On H_2 for 1 min after injection.
114	-	-	-	Run abandoned.
115	770	"	4.40	On H_2 for 3 mins after. Still poor end-point.
116	780	"	4.56	On H_2 for 5 mins after.
117	780	"	5.30	As 116.
118	790	"	4.92	On H_2, 15 mins before and after.
119	790	"	4.23	As 118.
120	840	"	4.7	Very poor end-point.
	Installed steam supply in bypass line.			
121	900	"	2.9	Instability in steam line.
122	780	"	3.12	On H_2 15 mins before and after.
123	780	"	3.94	As 122, slow flow of gas after.
124	850	"	4.48	Coal injection too rapid - tar.
125	820	"	3.83	As 124.
126	850	"	3.44	No steam at injection. H_2S came through when turned on later.
	Installed bypass tube heater.			
127	840	"	3.55	On H_2 10 mins before and after.
128	850	"	3.63	" " 10 mins before, 5 after.
129	855	"	4.3	Larger steam flow.
130	840	"	3.64	Much greater steam flow.
131	830	"	4.15	As 130.
132	830	"	4.17	As 131. Used pure steam in subsequent
133	840	"	3.2	As 132. /runs.
134	850	Dauntless 52/60	4.4	High superheat.
135	810	"	3.6	As 134.
136	800	"	3.8	As 135.
137	750	"	4.3	Very slow injection.
138	780	"	4.9	More steam.
139	780	"	-	Blockage.
140	850	"	4.3	As previous runs.
141	860	"	4.6	On H_2 5 mins after.
142	880	"	3.0	On H_2 3 mins after.
143	890	"	4.0	On H_2 5 mins after.
144	870	"	(4.8)	Analytical errors.
145	830	"	(4.2)	" "
	Replaced silica chips with ceramic beads.			
146	880	"	3.95	Lot of tar. Poor end-point.
147	880	"	4.27	2 absorbers in series. No react. in 2nd
	Replaced with fresh silica chips.			
148	830	"	3.63	As previous runs.
149	850	"	3.77	As 148.
150	850	"	4.28	Rapid injection.
151	840	"	2.56	As 150. Lot of tar produced.
152	850	"	4.67	Slow injection.

End of Series I.

Experiments - Series II

Trial Runs

Runs 153 to 167 in Hydrogen

153	830	Dauntless 52/60, trial run.
154	740	Stockton 52/60, top off, observation of behaviour.
155	820	" " trial run. Blockage.
156	790	" 85/100. Blockage.
157	700	" " . Agglomeration.
158	810	Dauntless 52/60. Good sample produced.
		Installed screw feeder.
159	940	Dauntless 85/100. Frequent blockages.
160	845	" " . Coke settling in lines.
161	740	" " . Satisfactory operation.
162	740	Stockton 85/100. Rapid blockage.
163	680	Dauntless 85/100. Satisfactory.
		Wangaloa coal used in subsequent runs, up to run 199.
164	700	85/100. Coal sticking in feeder - too wet.
165	605	" As 164, but sample obtained.
166	530	" As 165.
167	430	" As 165.
168	730	" Total sulphur 3.33%.
169	610	" " " 3.68%

Main Runs - Wangaloa

Run	Temp.	Mesh	% Total S	% Ash	% Volatiles	% Moisture	% Vols Loss (V.M.)	% S Loss (V.M.)	% S Loss (ash)	% Vols Loss (ash)
Runs 170-173, 197-198 in hydrogen, remainder in nitrogen.							37.2	71.2		
170	735	60/72	2.16	10.83	12.7	3.2			80.85	57.26
171	740	"	2.21	10.85	12.2	3.2	37.6	70.5	80.45	57.35
172	630	"	3.00	9.50	20.3	0.5	28.2	54.7	70.06	50.55
173	530	"	3.50	8.11	24.8	2.7	26.2	45.7	57.52	41.19
174	605	"	3.48	8.15	20.7	2.3	29.9	49.3	58.16	41.50
175	780	"	3.19	11.09	11.1	2.7	38.0	57.7	72.60	58.39
176	705	"	3.28	9.40	16.1	2.3	33.8	54.5	66.27	49.97
177	485	"	3.97	6.96	27.6	3.0	23.8	38.1	42.98	30.62
178	540	100/120	3.43	9.48	22.6	3.4	31.1	51.7	63.37	47.38
179	485	"	4.50	6.62	36.6	2.0	13.7	23.0	30.02	22.27
180	445	"	4.67	6.04	40.4	2.2	8.34	15.8	19.74	14.28
181	440	85/100	4.51	5.83	37.5	1.8	10.6	20.7	16.96	7.60
182	520	"	4.10	7.02	30.0	1.0	19.5	34.5	38.59	24.23
183	590	"	3.64	8.23	23.1	0.5	26.4	46.2	54.33	36.21
184	635	"	3.47	8.90	23.8	2.5	27.5	49.1	59.22	41.45
185	685	"	3.34	9.21	19.6	1.2	30.4	52.8	62.69	43.61
186	725	"	3.05	9.71	17.4	1.5	32.6	58.2	67.77	46.81
187	775	"	3.08	9.93	14.4	2.4	36.0	59.6	67.95	48.11
188	390	100/120	4.95	5.83	45.0	2.4	0.9	3.5	11.49	10.99
189	425	"	4.86	6.00	41.9	1.7	5.0	9.1	16.31	13.67
190	490	"	4.41	6.81	34.6	2.1	16.5	26.9	33.40	24.59
191	570	"	3.94	8.02	27.4	3.2	26.3	41.7	49.56	36.80
192	615	"	3.71	10.49	24.6	2.9	28.3	45.0	64.77	52.98
193	725	"	3.24	9.90	18.2	4.6	36.0	57.4	66.60	49.85
194	330	"	5.06	4.78	47.4	2.5	-2.8	-1.3	-11.69	-9.76
195	345	60/72	4.95	5.53	43.6	2.6	0.9	1.0	9.51	11.33
196	420	"	4.49	6.45	33.1	1.9	15.8	23.1	30.81	24.72
197	430	" H_2	4.61	5.97	34.0	2.5	15.1	20.6	22.38	18.25
198	320	" "	5.05	5.16	41.7	1.8	3.2	1.9	1.49	4.60
"Coke"	925	60/72	3.85	9.48	nil	nil	43.9	54.4	61.68	50.44
"Coke"	925	85/100	3.85	9.35	nil	nil	44.5	56.5	58.21	44.50
"Coke"	925	100/120	3.91	8.53	nil	nil	43.2	55.0	54.70	40.91

Main Runs - Stockton (oxidised)

Run	Temp.	Mesh	% Total S	% Volatiles	% S Loss	% Volatiles Loss
199	340	60/72	1.39	31.7	-12.74	2.02
200	420	"	1.35	27.7	-3.36	7.52
201	485	"	1.33	20.7	7.27	15.79
202	545	"	1.14	15.8	25.20	20.75
203	760	"	1.43	12.6	Rejected. Large contamination with bed material.	
204	610	"	1.30	11.7	" " " " "	
205	730	"	1.10	20.1	23.89	16.43
206	660	"	1.01	13.2	35.73	23.15
207	870	"	0.90	9.3	45.22	26.49
208	340	85/100	-	-	Agglomeration - samples rejected.	
209	540	"	-	-	" " "	
210	760	"	-	-	" " "	
211	990	60/72	1.10	3.6	37.05	30.88
212	955	" H_2	0.84	3.1	52.18	31.24
213	1000	" "	0.88	2.4	50.26	31.74
214	510	"	1.47	19.2	-0.56	17.37
215	630	"	1.29	11.6	19.42	24.56
216	800	"	1.28	9.9	Rejected - badly contaminated.	
217	930	"	1.00	3.5	42.83	30.95
"Coke"	925	"	1.23	nil	32.17	33.40

Analyses of volatile matter, moisture content and total sulphur (Eschka method) according to B.S. 1016.

Experimental Runs - Series III

Runs 220-339 used Charming Creek coal (35/100 mesh).

Run	Temp.	Gas	% S	% Vols	% Ash	Residence time			
220	800	N_2	4.67	-	-	-	Mixture of fine and coarse particles in product.		
Installed slow (10 rpm) motor in screw feeder.									
221	750	"	-	-	-	-	Uniform product except for white particles.		
Repaired cracks in furnace tube with fire cement.									
222	860	"	-	-	-	-	Still some white particles.		
Painted interior of tube with sodium silicate.									
223	950	"	3.66	10.8	-	-	No obvious signs of combustion.		
224	850	"	3.74	8.7	-	-			
225	770	"	4.20	12.1	-	-		% S Loss	% Vols Loss
226	910	"	3.85	6.9	-	-			
227	940	"	2.72	13.8	1.8	1.5		69.5	40.1
228	840	"	3.40	17.8	2.4	1.5		61.5	37.4
229	710	"	3.64	26.5	5.9	1.5		50.9	28.5
230	580	"	5.08	36.8	2.1	1.0		25.4	17.7
231	640	"	-	-	-	1.0			
Constructed new furnace, 16" long x 2½ I.D.									
232	880	"	5.30	18.9	5.4	3		51.6	36.9
233	620	"	6.55	35.1	6.6	2		28.5	20.4
234	765	"	5.65	19.8	9.7	2.5		42.8	36.2
235	1005	"	4.70	12.7	10.9	3		57.2	41.3
236	500	"	6.6	44.7	3.1	2		5.1	5.7
"Coke"	925	"	5.2	nil	7.13	-			
237	1030	H_2	3.5	10.7	-	-		66.3	42.6
238	690	"	-	-	-	-			
239	965	-	-	-		-			
Constructed new furnace 4' long x 2½" I.D.									
240	880	N_2	4.37	13.0	6.35			57.5	39.0
241	765	"	4.62	18.5	7.40			53.6	36.8
242	1005	"	4.21	12.8	9.19			59.8	41.2
243	620	"	5.73	23.1	6.19			39.7	32.9
244	500	"	6.44	24.7	4.00			33.6	32.9
245	500	Vacuum	-	-	-				
246	620	H_2	5.43	18.5	6.75			45.7	36.8
247	765	"	4.08	9.8	7.44			63.1	43.5
248	880	"	3.66	7.6	8.74			67.3	44.8
249	1005	"	3.27	7.3	8.78			70.8	45.0
250	500	"	6.58	38.9	4.33			13.4	14.7
Installed Incoloy tube, inside furnace.									
251	500	Vacuum	6.40	37.8	4.07			17.8	16.5
252	620	"	4.86	20.1	6.51			53.9	35.6
253	765	"	4.14	13.6	9.13			59.9	40.5
254	880	"	4.79	9.3	9.73			55.8	43.7
255	1005	"	4.82	7.2	10.2			60.9	45.1
Modified Incoloy tube, for "equilibrium" runs.									
256	1005	N_2	3.82	9.7	12.05)				
257	880	"	4.18	10.0	12.01)	--air leaks			
258	765	"	4.47	9.2	14.24)				
259	620	"	4.52	11.2	13.35)				
260	975	Vacuum	-	-	-		Unsuccessful.		
261	880	N_2+H_2	3.09	6.5	10.72		H_2- 15 secs		
262	880	"	3.20	5.6	6.17		" 30 "		
263	880	"	2.67	4.6	11.0		" 1 min.		
264	880	"	1.82	4.0	9.47		" 3 "		
265	1005	"	1.72	2.3	6.73		" 3 "		
266	1005	"	2.06	2.3	10.54		" 1 "		
267	1005	"	2.63	3.2	7.06		" 30 secs		
268	1005	"	2.65	2.55	6.00		" 15 "		
269	765	"	2.71	6.1	10.58		" 3 min.		
270	765	"	3.11	5.4	9.07		" 1 "		
271	765	"	3.80	8.5	7.27		" 30 secs		
272	765	"	3.34	5.3	5.53		" 15 "		
273	620	"	3.23	8.3	8.41		" 3 mins		
274	620	"	3.63	7.85	6.82		" 1 "		
275	620	"	3.98	8.3	6.03		" 30 secs		
276	620	"	4.19	8.8	5.43		" 15 "		
277	925	N_2	4.31	3.5	7.13				
278	765	"	4.11	7.51	4.58				
279	880	"	3.00	5.18	5.16				
280	1005	"	2.90	3.34	5.60				
281	1005	N_2+H_2	2.48	0.16	7.84		H_2- 15 secs		
282	620	N_2	3.50	7.22	7.39				
283	880	N_2+H_2	3.45	4.23	4.98		H_2- 15 secs		
284	880	"	2.64	2.14	6.48		" 1 min.		
285	1005	"	2.56	3.03	5.13		" 1 "		
286	1005	"	2.07	4.88	5.06		" 3 "		
287	1005	"	2.97	2.00	5.22		" 30 secs		
288	765	"	2.33	2.29	5.32		" 3 mins		
289	765	"	2.82	3.29	4.65		" 1 "		
290	765	"	3.35	12.2	4.11		" 30 secs		
291	765	"	3.75	3.51	4.07		" 15 "		
292	620	N_2	4.57	7.28	1.67				
293	925	"	4.26	2.37	5.91				
294	620	N_2+H_2	3.85	7.38	4.61		H_2- 3 mins		
295	620	"	4.27	-	4.79				
296	620	"	4.32	-	7.75		" 30 secs		
297	620	"	4.48	-	7.30		" 15 "		
298	880	"	2.19	2.24	9.18		" 3 mins		
299	880	"	3.57	2.65	7.70		" 30 secs		
300	1005	"	3.59	-	7.81		" 15 secs		
301	880	N_2	4.23	-	5.55		Repeat of 232		
302	1005	N_2	4.41	-	7.16		Repeat of 235		
303	765	"	4.92	-	7.28		Repeat of 234		
304	620	"	5.22	-	6.01				
305	765	"	4.39	-	7.32				
306	880	"	4.29	-	5.78				
307	1005	"	4.37	-	7.45				
308	1005	N_2+H_2	3.80	-	8.47		H_2- 15 secs		
309	880	"	3.58	-	6.19		" 30 "		
310	880	"	3.04	-	4.63		" 1 min.		
311	880	"	2.16	-	6.83		" 3 mins		

Run	Temp.	Gas	% S	% Vols	% Ash	Residence time	SiO_2/SiO_2(coal)	Fe/Fe(coal)
Removed constriction from Incoloy tube.								
312	500	N_2	6.42	-	2.06	4 secs	1.28	0.72
313	620	"	5.30	-	3.45	10 "	2.53	1.51
314	765	"	4.59	-	3.78	14 "	4.26	0.77
315	880	"	4.11	-	3.85	15 "	3.97	1.06
316	1005	"	4.26	-	3.90	15 "	5.22	0.93
317	1005	"	4.51	-	3.82	10 "	2.90	1.88
318	880	"	4.35	-	4.00	10 "	2.93	0.90
319	765	"	4.42	-	3.85	9 "	2.34	0.81
320	620	"	5.18	-	3.45	6 "	2.66	0.96
321	500	"	6.31	-	2.47	2 "	1.48	0.43
322	500	"	6.45	-	2.41	0.8 "	0.98	0.35
323	620	"	5.83	-	3.22	1.5 "	2.10	1.50
324	765	"	4.55	-	3.80	2.5 "	2.79	1.27
325	880	"	4.28	-	4.16	3 "	-	1.19
326	1005	"	4.11	-	4.32	3 "	-	1.20
Replaced constriction in Incoloy tube.								
327	765	"	4.10	-	4.08		2.39	1.77
328	765	N_2+H_2	3.76	-	3.98	H_2- 30 secs	2.60	1.35
329	765	N_2+H_2	3.08	-	3.96	"- 1.5 mins	3.03	2.63
330	765	"	3.14	-	4.34	" 5 mins	1.88	3.35
331	880	N_2	4.22	-	4.81		2.30	2.77
332	880	N_2+H_2	3.68	-	4.77	H_2- 30 secs	2.30	1.64
333	880	N_2+H_2	2.94	-	4.87	"- 1.5 mins	2.60	2.47
334	880	"	2.34	-	5.02	" 5 mins	2.18	5.38
335	1005	N_2	3.89	-	4.81		2.83	5.84
336	620	"	5.08	-	3.60		3.41	2.37
337	620	N_2+H_2	4.74	-	3.17	H_2- 30 secs	2.75	2.01
338	620	N_2+H_2	4.30	-	-	"- 1.5 mins	3.03	2.22
339	620	"	4.85	-	-	" 5 mins	4.22	2.13
"Coke"	925	-	5.20	0.00	6.95			

END OF EXPERIMENTS WITH CHARMING CREEK COAL

Runs 340-423 used either Wangaloa 85/150 mesh, or Dauntless 85/120 mesh.

Run	Temp.	Gas	
340	500	N_2	Air leaks
341	600	"	" "
342	600	"	" "

Installed new Incoloy DS tube, together with two more furnaces.

343	500	"	
344	600	"	
345	720	"	Rejected because of scale contamination.
346	820	"	
347	900	"	

Runs 348-377: Wangaloa coal.

Run	Temp.	Gas	% Loss of Wt	% S	% Vols	% Ash	Residence time	%Vols Loss (actual d.a.f.)	% S Loss (actual)	% S Loss (V.M.)	% Vols Loss (V.M.)	% S Loss (ash)	% Vols L (ash)
348	900	N_2	60.7	2.89	8.9	10.27	12 secs	62.5	78.7	67.7	46.3	87.6	81.8
349	810	"	57.0	2.90	14.7	9.67	12	61.1	77.9	65.4	42.2	86.8	79.5
350	700	"	53.8	3.02	19.4	8.85	11	55.8	74.1	62.2	38.5	85.4	77.9
351	600	"	48.0	3.32	25.0	8.17	10	50.1	68.1	55.8	33.5	82.8	75.8
352	490	"	35.2	4.31	33.0	6.57	7	37.4	49.4	37.8	25.2	73.5	69.4
353	390	"	9.0	5.35	47.7	4.83	5.5	11.3	12.0	1.8	2.8	56.2	57.7
354	395	"	10.6	5.28	46.4	4.95	7	12.9	14.5	5.48	5.3	57.7	58.7
355	495	"	37.0	4.45	30.7	6.82	9	39.2	48.5	37.1	27.7	73.4	70.6
356	600	"	48.0	3.44	21.9	8.34	13	50.2	66.9	57.8	36.3	82.7	76.6
357	710	"	53.9	3.12	14.0	9.33	15	56.1	73.3	63.1	42.8	85.8	79.1
358	820	"	58.5	2.97	8.1	9.96	16	60.1	77.0	67.2	46.8	87.0	80.6
359	910	"	63.7	3.21	6.65	10.65	16	65.5	78.1	65.0	47.7	86.8	81.9
360	900	"	59.7	3.21	8.37	10.5	10	61.8	75.7	64.3	46.6	86.7	81.7
361	800	"	56.2	3.04	11.2	10.1	10	58.5	75.2	65.1	44.7	86.7	80.8
362	690	"	52.3	3.25	16.9	9.14	9	54.6	71.3	60.7	40.5	84.8	78.7
363	605	"	48.7	3.60	22.6	8.68	8	51.0	65.9	53.5	35.7	82.5	77.4
364	505	"	38.1	4.40	30.2	7.30	6	40.5	50.1	38.1	28.2	74.3	72.7
365	410	"	12.5	5.18	45.7	4.95	4	14.7	17.7	8.3	6.6	58.4	58.7
366	375	"	5.6	5.38	47.5	5.20	2.5	8.3	8.0	0.9	3.0	58.9	60.8
367	530	"	32.8	4.35	36.2	6.30	4	35.3	46.7	34.4	22.7	74.0	70.5
368	605	"	45.6	3.86	25.1	8.19	5	47.9	61.2	48.8	33.3	80.3	75.9
369	690	"	49.9	3.26	21.0	8.74	6	52.2	69.8	58.6	37.1	84.0	77.5
370	790	"	53.8	3.15	15.5	9.62	6.5	56.1	73.0	62.3	41.6	85.8	79.8
371	885	"	58.5	3.06	12.1	10.2	6.5	60.6	76.3	64.5	44.0	86.7	81.1
372	900	"	56.7	3.32	10.2	10.6	3.5	59.1	73.2	62.5	45.4	86.4	81.9
373	775	"	52.2	3.15	13.6	10.2	3.5	54.9	72.0	62.9	43.0	86.5	81.1
374	685	"	48.8	3.28	18.2	9.52	3.5	51.6	68.9	59.4	39.4	85.2	79.6
375	595	"	43.5	3.71	27.0	8.38	3.0	46.1	61.5	49.1	31.3	81.5	76.5
376	500	"	28.5	4.47	35.5	6.71	2.5	31.1	41.7	32.0	21.8	72.9	70.1
377	385	"	6.5	5.24	46.9	4.94	1.5	9.0	11.2	5.0	4.4	57.9	58.7
COKE	925	-	50.5	3.86	NIL	9.16	7 mins	52.9	64.6	61.5	51.6	82.3	78.7

Runs 378-407: Dauntless coal.

378	900	"	71.5	5.76	5.9	8.07	16 secs	65.5	71.9	57.3	47.7		
379	800	"	70.8	5.25	9.9	7.53	16	64.6	71.1	58.8	45.2		
380	710	"	67.6	5.02	13.2	7.19	15	61.5	72.4	59.1	42.8		
381	610	"	62.1	5.38	19.8	5.86	12	55.9	66.7	53.0	38.0		
382	490	"	48.3	6.96	31.2	3.44	8	41.4	44.1	31.0	27.6		
383	395	"	10.8	7.35	51.7	2.09	6	3.9	4.6	-3.4	-4.0		
384	390	"	10.8	7.16	51.4	3.73	5	5.1	6.5	-3.2	-5.0		
385	500	"	52.5	6.60	26.8	5.00	6.5	46.2	50.6	37.3	31.8		
386	615	"	62.0	5.42	18.0	6.00	9.5	55.7	66.2	53.8	39.4		
387	700	"	66.4	5.18	13.3	6.74	12	60.2	70.7	58.0	42.8		
388	800	"	68.6	5.68	6.9	7.25	13	62.5	69.6	57.0	47.1		
389	905	"	70.5	5.63	4.1	8.33	13	64.6	71.2	58.2	48.7		
390	900	"	69.7	5.40	6.4	8.86	9.5	64.1	71.9	58.7	47.3		
391	800	"	67.9	5.79	8.5	6.71	9.5	61.6	68.5	55.7	46.1		
392	710	"	65.1	5.70	12.4	7.21	9	59.2	66.8	54.2	43.4		
393	600	"	59.7	5.87	21.6	8.20	7	54.7	61.7	45.9	35.9		
394	480	"	36.4	6.38	39.4	4.06	4.5	30.3	38.6	26.7	16.8		
395	400	"	9.7	6.78	51.6	4.02	4	4.7	10.9	0.8	-6.0		
396	410	"	9.3	6.58	51.3	4.09	3	4.4	13.1	5.0	-5.5		
397	505	"	42.7	6.20	35.3	6.58	3.25	38.1	45.7	30.8	21.2		
398	600	"	59.3	6.29	23.1	6.79	5	53.6	58.5	41.8	34.8		
399	700	"	62.7	6.41	15.5	6.88	6	56.9	60.7	46.4	41.2		
400	805	"	66.1	6.06	9.8	7.28	6.5	60.2	65.5	52.5	45.2		
401	900	"	68.0	5.72	6.2	5.98	6.5	61.4	68.9	57.8	47.6		
402	885	"	68.3	5.71	4.0	7.84	3.5	61.4	68.4	58.2	48.8		
403	810	"	65.6	5.66	9.6	8.62	3.5	60.2	67.3	55.1	45.3		
404	695	"	61.5	6.01	18.8	7.87	3	56.1	62.1	46.8	38.4		
405	595	"	53.5	6.23	24.5	7.18	2.5	40.4	47.2	40.9	33.3		
406	500	"	40.1	6.94	37.3	7.92	2.0	36.5	36.7	18.0	17.7		
407	410	"	8.5	7.26	51.5	7.45	2.0	6.9	3.4	-14.4	-10.4		
COKE	925	-	56.7	5.91	NIL	4.8	7 mins	50.2	59.1	61.6	51.0		

Runs 408-423 were "equilibrium" runs, with constriction in place.

408	400	"	20.0	5.07	42.4	5.38	equilibrium	22.15	24.2	14.8	12.2	Wangaloa	
409	400	"	18.4	7.38	48.9	3.02	"	12.1	11.3	5.3	1.2	Dauntless	
410	500	"	45.2	3.98	22.0	7.88	"	47.35	67.7	49.3	36.3	Wangaloa	
411	500	"	56.4	6.97	21.8	6.01	"	50.5	51.4	37.4	36.2	Dauntless	
412	600	"	51.2	3.75	17.1	9.25	"	53.55	63.0	54.3	40.3	Wangaloa	
413	605	"	63.3	5.72	13.3	6.91	"	57.4	65.4	53.6	42.8	Dauntless	
414	710	"	58.2	2.90	7.4	9.87	"	60.15	75.2	68.2	47.3	Wangaloa	
415	700	"	68.2	5.27	8.2	5.17	"	61.3	71.6	61.9	46.5	Dauntless	
416	805	"	62.9	3.17	4.1	10.65	"	64.7	75.7	66.1	49.25	Wangaloa	
417	810	"	69.6	5.46	3.99	4.95	"	62.5	71.5	61.3	48.9	Dauntless	
418	900	"	65.5	3.28	3.42	11.0	"	67.15	76.4	65.0	49.6	Wangaloa	
419	910	"	71.1	5.78	2.92	8.24	"	65.1	70.9	57.8	49.4	Dauntless	
420	900	N_2+H_2	-	2.07	-	11.55	"	Hydrogenated for short				Wangaloa	
421	900	"	-	2.69	-	11.75	"	periods. Runs discontinued				"	
422	900	"	-	2.77	-	11.44	"	due to explosion hazard.				"	
423	900	"	-	2.48	-	11.72	"					"	

Smoothed Data: Wangaloa and Dauntless Runs

	Wangaloa				Dauntless			
Temp.	Time	% Vols Loss (actual d.a.f.)	% Sulphur (d.a.f.)	% S Loss (actual)	Time	% Vols Loss (actual d.a.f.)	% Sulphur (d.a.f.)	% S Loss (actual)
400	1.5secs	12.0	5.46	15.0	2 secs	2.0	7.87	2.0
"	2.5	13	5.50	15.3	3	1.0	6.92	9.3
"	4	14.65	5.50	16.9	4	4.7	7.07	10.8
"	5.5	13.0	5.50	15.3	5	10.0	7.40	11.8
"	7	13.5	5.50	15.9	6	7.0	7.50	7.7
500	2.5	31.1	4.79	41.7	2	36.5	7.54	36.6
"	4	33.5	4.83	43.2	3.25	37.5	6.65	45.0
"	6	40.0	4.80	49.1	4.75	36.0	6.62	44.0
"	7	38.5	4.50	51.2	6.5	46.2	6.94	50.6
"	9	39.8	4.74	49.6	8	43.5	7.05	47.3
600	3	46.5	4.00	62.2	2.5	41.5	6.68	48.3
"	5	47.5	4.24	60.7	5	53.6	6.75	58.5
"	8	50.5	3.98	65.2	7	54.7	6.38	61.7
"	10	50.1	3.62	68.0	9.5	54.0	5.85	64.4
"	13	50.15	3.76	66.9	12	55.5	5.80	65.8
700	3.5	52.3	3.59	69.8	3	56.5	6.50	62.6
"	6	52.8	3.49	70.9	6	56.9	6.88	60.8
"	9	55.0	3.56	71.7	9	58.8	6.16	66.5
"	11	55.75	3.31	74.1	12	60.2	5.56	70.7
"	15	55.9	3.48	72.9	15	61.0	5.45	71.8
800	3.5	55.7	3.50	72.6	3.5	60.0	6.18	67.3
"	6.5	56.5	3.48	73.2	6.5	60.1	6.58	65.2
"	10	58.5	3.38	75.2	9.5	61.6	6.21	68.5
"	12	60.8	3.21	77.7	13	62.5	6.13	69.6
"	16	59.8	3.28	76.7	16	64.6	5.68	73.4
900	3.5	59.1	3.71	73.1	3.5	61.9	6.20	68.7
"	6.5	61.2	3.41	76.6	6.5	61.4	6.08	68.9
"	10	61.75	3.59	75.7	9.5	64.1	5.92	71.9
"	12	62.5	3.22	78.7	13	64.4	6.15	71.0
"	16	65.0	3.50	78.3	16	65.5	6.17	71.8
400	Equilibrium	22.15	5.35	26.4	Equilibrium	12.1	7.61	11.3
500	"	47.35	4.32	59.8	"	50.5	7.42	51.4
600	"	53.55	4.13	66.1	"	57.1	6.19	64.8
700	"	60.1	3.26	77.0	"	61.3	5.55	71.6
800	"	64.4	3.50	78.0	"	62.4	5.71	71.5
900	"	67.15	3.69	78.6	"	64.5	6.25	70.7

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